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New Metallosupramolecular Assemblies Involving Silver-Alkene Interactions

A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy in Chemistry

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Abstract

This thesis describes the silver(I) coordination chemistry of forty two ligands containing alkene functional group. The synthesis of thirty nine ligands is described, fourteen of which were previously unreported compounds. These ligands are classified into three major categories containing allyloxy, diallylamine and allyl groups.

The ligands containing allyloxy groups were designed by changing the number of allyloxy arms from one to six, which allows investigation of the influence of the number of allyloxy arms within a ligand on the overall structure of the complex. Ligands containing one allyloxy arm generally form rectangular shaped discrete assemblies that involve the coordination of the nitrogen atom of the core and the allyloxy arm of the ligand with silver. Ligands containing two and three allyloxy arms gave 1D and 2D polymeric structures. Some of these 2D polymers contain cavities filled by the counter anion and the solvent used to grow crystals of the complex. Some of the ligands containing four allyloxy arms gave discrete M_2L or M_4L_2 type coordination complexes. One of these ligands gave a rare type of 1D-1D polycatenane by intercalating two ladders. A ligand containing six allyloxy arms forms a 1D polymeric assembly by using the six allyloxy arms and four silver atoms. Four of these allyloxy arms chelated, while the other two are bridging.

Ligands containing two, four and six allyl arms were designed by using diallylamine groups. Introducing additional functional groups in the core structure of the ligand showed the co-existence of silver(I)-alkene interactions with other strong interactions, such as silver(I)-nitrogen. Ligands containing one diallyamine group with different silver(I) salts resulted in 1D polymeric assemblies, while two and three diallylamine groups inclined to form M_2L, M_3L and M_4L_2 discrete assemblies.

Ligands containing allyl groups with a urea core structures showed the coexistence of silver(I)-alkene interaction with other moderate interactions such as silver(I)-carbonyl oxygen. The use of ligands containing allyl group allowed the formation of 1D polymeric ladders and helical structures as well as discrete assemblies.

^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, mass spectrometry, IR, melting point and X-ray crystallography were used to study the compounds synthesised. The crystal structure of six ligands, forty-six complexes and two salts are discussed.

Chapter one

Introduction

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1.1 Supramolecular chemistry

Supramolecular chemistry[1] is a relatively new and growing branch of chemistry. Jean-Marie Lehn, 1987 Nobel prize winner in chemistry,[2] defined supramolecular chemistry as the "chemistry of molecular assemblies and of the intermolecular bond", or as "chemistry beyond the molecule".[1, 3-4] This definition expresses how individual molecules recognise, associate and interact with each other to generate a new larger entity.

Traditional chemistry focused on the step-wise construction of molecules from individual atoms using covalent bonds as a 'glue' to hold the components together. The covalent bonds between the atoms are usually strong and hard to break. In contrast, supramolecular chemistry involves the use of non-covalent interactions to hold together assemblies of molecules, where these weaker non-covalent interactions consist of such interactions as hydrogen bonding, van der Waals interactions, electrostatic interactions and π-π stacking interactions, as shown in Figure 1.1.[5]

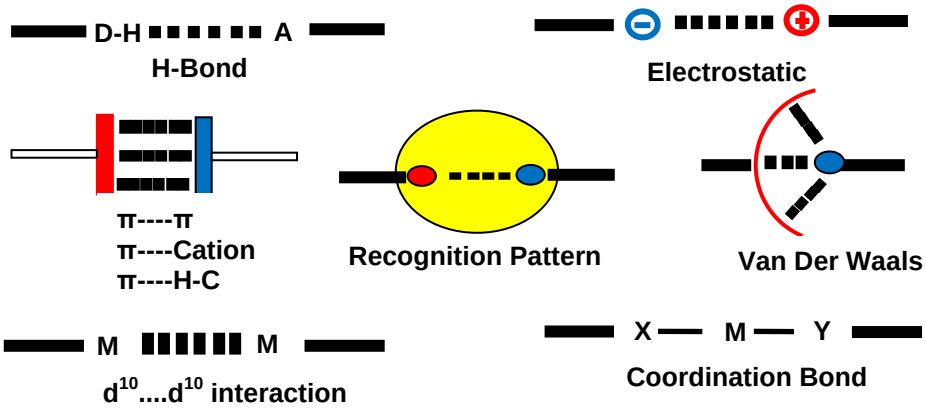


Figure 1.1 *– Types of non-covalent interactions involved in supramolecular chemistry.*[5]

Supramolecular synthesis utilises the whole molecules as 'building blocks' and the weak non-covalent intermolecular interactions as 'glue' to build large

molecules through self-assembly process. These intermolecular interactions are weak relative to the covalent bonds, but the additive effect of many interactions can have a profound influence on the stability of the structure. These weak interactions, by easily breaking and reforming, allow the formation of a thermodynamically stable product that allow the system to pass through an error checking phase until the most stable assembly is formed.[5-6]

Nature is the model for artificial supramolecular processes.[7] Inter- and intramolecular non-covalent interactions are of major importance for most biological systems such as highly selective catalytic reactions and information storage; different non-covalent interactions are present in proteins, giving them their specific structures.[8] DNA represents one of the most famous examples, where the self-recognition of the complementary base-pairs by hydrogen bonding leads to the self-assembly of the double helix.[9] Hydrogen bonding usually occurs between hydrogen atoms (donor atoms) and electronegative atoms (acceptor atoms). They are relatively weak, in the order of 5-30 $kJmol^{-1}$ and are usually directional.[10-11] Hydrogen bonding has been utilised for the formation of discrete assemblies and polymeric arrays in the literature.[12-13]

One of the most common interactions observed in supramolecular assemblies involving aromatic rings, is π-π stacking between the aromatic rings.[14] π-π interactions occur in two ways, the first is a partial overlap of parallel rings, typically at an interplanar distances of 3.4 Å to 3.8 Å[15-18]and slightly offset or ‘slipped’ to maximise the electrostatic interaction, with the strongest interaction takes place between π-polarised systems or by alternating π-rich and π-poor systems.[17] This interaction is known as a face-to-face π-π interaction. The second type of interaction is known as an edge-to-face π-π interaction.[19-20] As the name suggests the edge of one of the aromatic rings interacts with the face of the second.

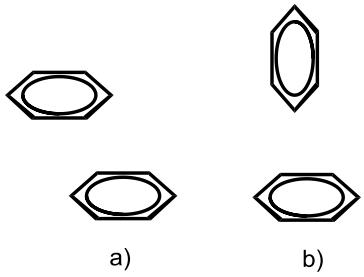


Figure 1.2 *– The two types of π-π interactions between two aromatic rings. a) Face-to-face and b) edge-to-face π-π interactions.*

1.2 Metallosupramolecular chemistry

In 1994, Constable coined the term “metallosupramolecular chemistry” to describe discrete or polymeric assemblies which contain organic molecules (ligands) held together by metal atoms.[21-22] The coordination bonds that are formed between the metal atoms and the organic compounds act as a supramolecular ‘glue’, which binds the building blocks together.[7-8] This leads to more robust structures, as the interactions between the metals and ligands are generally strong. However, the strength depends on the nature of the metal and the ligand used, and it can range from very weak to very strong.[23] In addition to being surprisingly straight forward and simple chemistry, the self assembly of metallosupramolecular assemblies leads to the formation of novel and interesting structures.[24-25] A fantastic range of structures have been constructed by incorporating metal atoms and organic ligands, such as polygons,[24, 26-27] knots, [28-30] rotaxanes,[31-33] catenanes,[29, 31, 34] and helicates.[35-38]

Metallosupramolecular chemistry involves the interplay of thermodynamic and kinetic factors, in which the building blocks interact with one another. Consequently, this interplay depends on the original properties of the building blocks or on the properties of the metal salts and the organic ligands involved. This dependence has a tremendous advantage in that the designing of a particular metallosupramolecular assembly can be achieved in a controlled manner, by choosing an appropriate metal and organic ligand.

To obtain a desired product, encoding complementary information into both the ligand and a metal atom is a strict prerequisite for the self assembly process of the components into a single product.[4] To achieve this, the metal atom must have certain lability towards the desired thermodynamic product over the kinetic products and also should have a preferred geometry. These two factors should be considered during the choice of the metal atom for a particular metallosupramolecular assembly.

Metals chosen for metallosupramolecular assemblies usually have their own preferred coordination numbers and geometries. The most common coordination geometries of the metal atoms are shown in Figure 1.3.

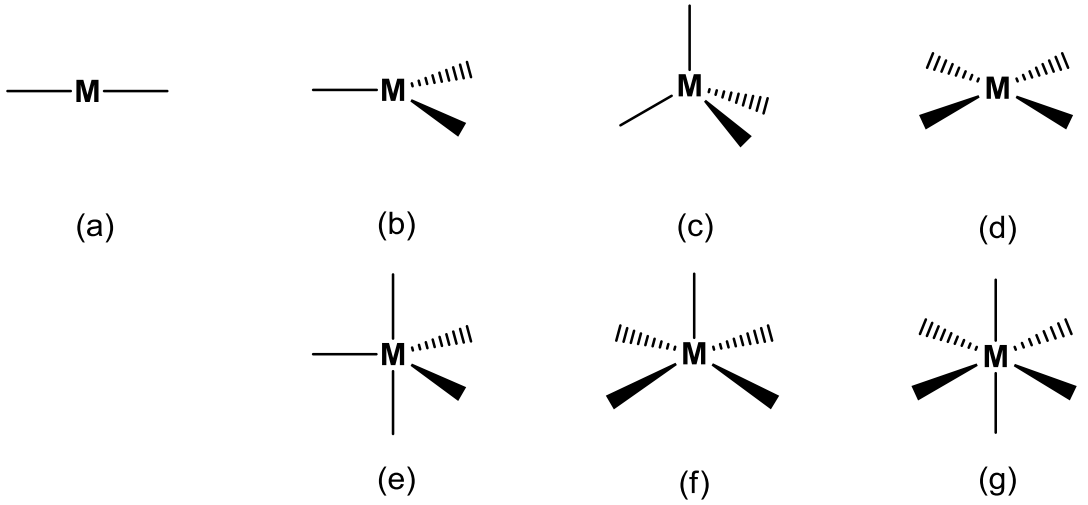


Figure 1.3 *– Some of the possible coordination geometries formed by metal atoms in different metallosupramolecular assemblies. From left to right: linear, trigonal planar, tetrahedral, square planar, trigonal bipyramidal, square pyramidal and octahedral.*

Silver(I) is a d^{10} metal, flexible in its choice of coordination number and geometries, often with coordination numbers varying from 2-8. However, the lower coordination numbers are most common, with linear and various three and four coordinate geometries being predominant.[39] Metal atoms with other electron configurations of d-electrons have more strict preferences for coordination numbers and geometries than silver(I). For instance, copper(II) with d^9 electron configuration usually forms trigonal bipyramidal or square

pyramidal geometries. The divalent d^8-metal palladium(II) has a strong preference for square planar coordination geometry.

The choice of the counter anion must also be taken into account during the choice of the metal atom. The non-coordinating type anions, such as tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-), are not usually coordinating with the metal atom during the metallosupramolecular assembly; therefore, there will be a free coordination site around the metal for the ligand to interact. However, the non-coordinated anion needs free space in the crystal lattice which fits with its size and as a result of this the non-coordinating anions can often be disordered. The coordinating type anions such as nitrate (NO_3^-), triflate ($SO_3CF_3^-$) and perchlorate (ClO_4^-) anions interact with the metal in a chelating, bridging or terminating manner, occupying a coordination site on the metal; therefore, the geometry and the coordination number of the metal will be affected.

In addition to the type of metal and the counter anion used, the number and type of the donor group as well as the geometry of the ligand has to be considered. The ligand can have as much influence as the metal on the overall structure of the metallosupramolecular assembly. Ligands can have multiple donor groups and various bridging capabilities that increase the complexity of the resulting structure. In order to maintain the thermodynamic control over the kinetic one, it is necessary to keep in mind the lability of the ligand and the metal atom.

The design of the ligand can control the geometry as well as the separation distance between the metal atoms of the structure. As shown in Figure 1.4, ligands can accommodate different geometries that lead to different types of metallosupramolecular assemblies.

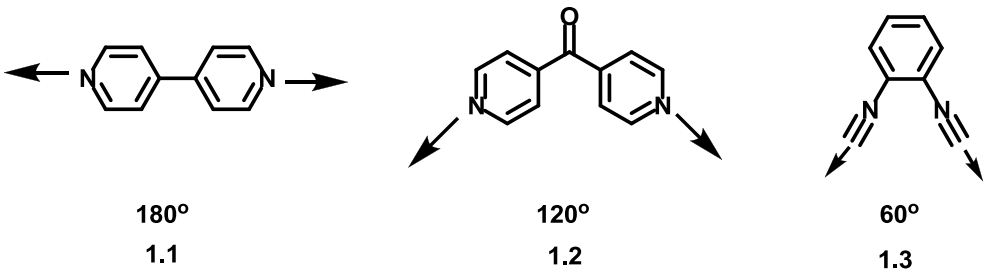


Figure 1.4 *– Geometries available through some organic ligands.*

Combinations of a linear ligand like compound **1.1** in Figure 1.4, with a metal atom that can provide, a two coordinate, 180° linkage will result in a linear polymeric structure. Combinations of a linear metal atom with a non-linear ligand will result in a zig-zag shaped polymer. This methodology can extend to the formation of two- and three-dimensional polymeric assemblies.

Discrete assemblies can also be accessible through metallosupramolecular chemistry. For instance, molecular squares can be assembled by using a 90° metal corner and a linear linker like ligand **1.1**.[40-43] The corners of the structure can be assembled from the ligand molecules. For example, Stang *et al.* showed the construction of a simple hexagonal assembly by using ligand **1.2** as the 120° angle corner of the hexagon and ligand **1.1** as linear linker combined with a 180° metal center that connects the corner with the linker species.[40, 44] Espinet *et al.* showed the assembly of a metallotriangle by using ligand **1.3** as a 60° angle corner of the triangle and a linear 180° metal as a linker.[40, 45] The metal atoms can also be used as corners and the organic ligands as linkers for different metallosupramolecular assemblies.

Ligands used in the metallosupramolecular chemistry can be varied in many ways, but all of the ligands must contain at least one or more donor groups or coordinating sites that could interact with the metal. In most metallosupramolecular assemblies nitrogen-containing ligands, particularly nitrogen-containing heterocyclic compounds, are used. Nitrogen is used because it forms relatively strong bonds with most of the transition metals. For example, the nitrogen in pyridine has a lone pair, which can donate to the metal. As the pyridine π system is electron deficient it can also accept

electron density back from the metal,[46] therefore there is partial double bond character thus giving a relatively strong bond between the metal and ligand.

The donor atoms or groups are not limited to nitrogen atoms, as shown in Figure 1.4, but also other heteroatom ligands that contain oxygen,[47-48] phosphorous,[49-50] and sulfur.[51] In this project, alkene functional groups are used as donor or coordination sites.

1.3 Metal-Alkene interactions

The first metal-alkene complex was reported in the early 1800's by William Christopher Zeise, which consists a platinum salt of one coordinated ethylene molecule and three coordinated chlorines.[52] However, the X-ray structure of the salt was not determined until 1954[52-53] and the most definitive study was carried out by neutron diffraction later on.[52, 54] As shown in Figure 1.5, the complex is a square-planar platinum salt consisting of three coordinated chlorines and one coordinated ethylene molecule, with each carbon atom equidistant from platinum, and a potassium counter cation; $K[(C_2H_2)PtCl_3]$. This salt is known as Zeise's salt.[52]

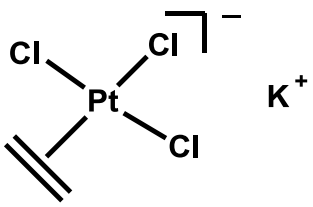


Figure 1.5 *– Zeise's salt.*

Since then a number of transition metal-alkene complexes have been reported, especially with group 10 transition metals (nickel, palladium and platinum).[55] In general the alkene interacts with the metal in a η^2-manner, in which the alkene group usually orients perpendicular to the coordination plane of the metal, as shown in Figure 1.6.

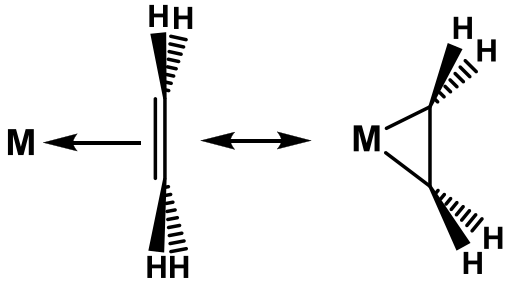


Figure 1.6 *– Resonance contributors to the structure of an ethene-metal complex.*[56]

In 1951 Dewar proposed the correct bonding picture for metal-olefin complexes as a normal dative bond.[57] This would occur through the overlap of the filled π-molecular orbitals of the alkene C=C bond with a vacant metal orbital of corresponding symmetry, accompanied by backbonding through the overlap of the π* antibonding orbitals of the olefin C=C bond and a filled d-orbital of the metal, which has the appropriate symmetry.[52, 57] Dewar proposed this concept using an Ag^{+}-olefin complex, but later on Dewar mentioned the olefin complexes of nickel and platinum. Slight modification of the model by Chatt and Duncanson by applying to other transition metals, lead the model to be known as the Dewar-Chatt-Duncanson model.[58-59]

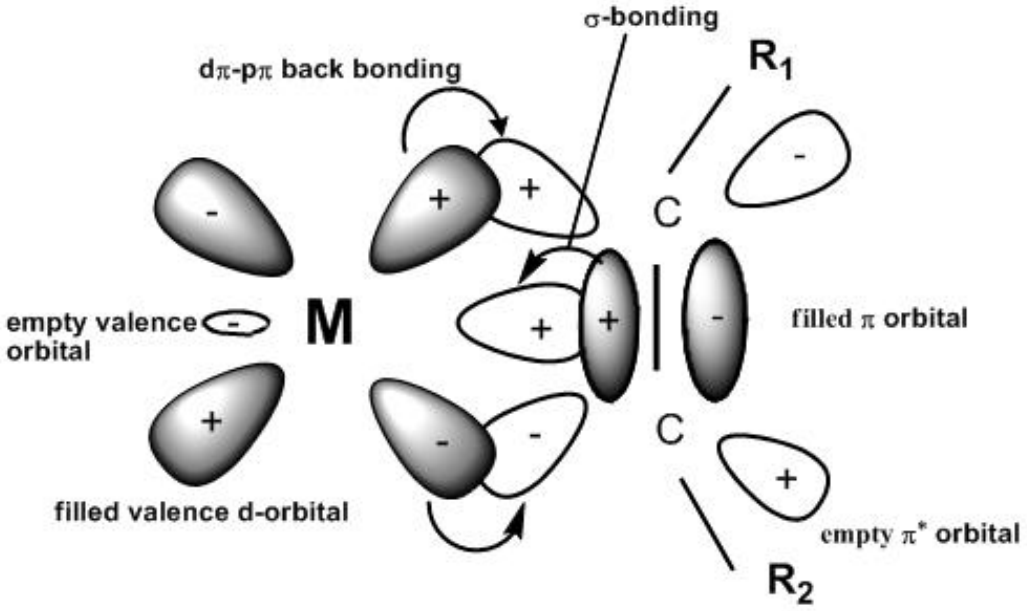


Figure 1.7 *– Orbital description of metal-alkene bonding.*[60]

Computational studies done by Ziegler *et al.*[61] and then by Hertwig *et al.*[62] indicate that back-donation plays a more significant role in the bonding between olefins and first row transition metals than it does in the second and third row. Calculations, carried out by Bowers *et al.*,[63] showed that the dominant bonding interaction is donation from the π-orbital of the alkene functional group to the 5s orbital of the Ag^+, while the populations of the 4d-orbitals of Ag^+ remain mostly unchanged when bound to the alkene functional group, indicating that back-donation from the 4d-orbitals of the Ag^+ to the π^* antibonding orbital of the alkene is minimal, hence back-donation does not play a big role in the silver-alkene interaction.

1.4 Silver-Arene interactions

Silver-arene complexes were first described by Hill during the course of phase studies in the early 1920's.[64-65] Nearly three decades later, more significant work was reported on silver-arene interactions.[66-67] Silver(I) can interact with aromatic rings such as benzene in an η^1,[68-70] η^2,[67, 71] η^3,[72-73] or η^6 [74-76] manner, with η^2 being the most common.

The η^2-type interaction of silver(I) with the aromatic ring caused slight elongation of the bond length of the two carbon atoms involved in the interaction.[77] The electron density reduction around the two carbon atoms by silver(I) due to the η^2-fashion interaction has been suggested as a reason for the slight elongation of the bond length of the carbon atoms involved in the interaction.[77] Conversely, others reported the shortening of the bond lengths of the two carbon atoms.[67, 78] Two reasons have been given for the shortening of the C-C bond lengths: the distortion of the molecular planarity of the aromatics[78] or polarization of the π-bonding system by the silver(I) leads to an increase in electron density.[67] Others reported that no significant distortion of the aromatic system at all.[79]

Munakata *et al.* used silver-arene interactions, especially η^2-type interactions extensively in metallosupramolecular chemistry to construct different frameworks such as double-layer, triple-layer, pillared brick, W-type architecture, multilayer and herringbone multilayer assemblies in sandwiched

silver(I) aromatic systems.[80-81] Most of the silver-arene interactions observed in this project are η^1 and η^2-types.

1.5 Silver-alkene interactions

Silver(I)-alkene complexes have been known since the 1930s.[82] In the 1960s and 1970s there were many simple silver(I)-olefin complexes that were characterised in both solution and solid state by NMR and IR respectively.[83-84] The first silver-ethene complexes, which resulted in $Ag(C_2H_4)_n^+$ salts (n=1,2,3), were prepared from the reaction of solid silver(I) tetrafluoroborate and gaseous ethene.[83] Numerous experimental and theoretical investigations have been conducted in order to ascertain the nature of the interaction between silver and these small alkenes.[85-86] Experimental bond dissociation energies (BDEs) of $Ag(C_2H_4)_n^+$ have been measured by Manard *et al.* and are 32.2, 30.1, 13.6, 6.5 and 4.4 kcal/mol for n = 1‑5, respectively, with the BDE of the sixth ligand estimated to be 3.3 kcal/mol,[87] values that agree with the computational studies.[88] These studies show that the strength of silver-alkene interactions decreases for each subsequent addition of ethene and for n>3 are not stable.

There are examples of silver(I) complexes with ethene, which have been characterised by single crystal X-ray crystallography.[89-91] Silver(I) complexes containing ethylene are rare, as ethylene is easily displaced by weakly donating species and additional supporting ligands, which are generally highly fluorinated and weakly coordinating, such as the highly fluorinated tris-pyrazolylborates,[90, 92] or diazapentadienyl ligands[93] are required to stabilise these complexes. The structure of the first stable tris‑ethene adduct, which is prepared as a salt with the $[Al\{OC(CF_3)_3\}_4]^-$ anion, as shown in Figure 1.8, was reported by Reisinger *et al.*,[56, 94] Interestingly, the three ethene ligands all lie in the coordination plane, rather than perpendicular to it.

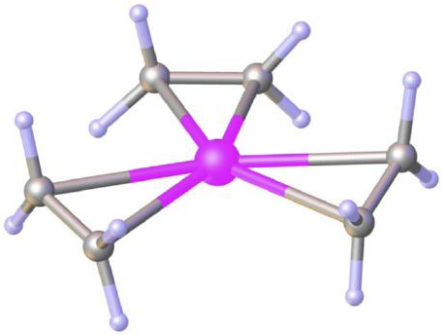


Figure 1.8 *– The cation in the first tris-ethene-silver complex.*[56]

There are numerous compounds, containing alkene functional groups, which act as ligands for silver(I) and their crystal structures have been determined for various reasons. This group of compounds includes natural products, strained or unusual hydrocarbons, annulenes and crown ethers, as shown in Figure 1.9.

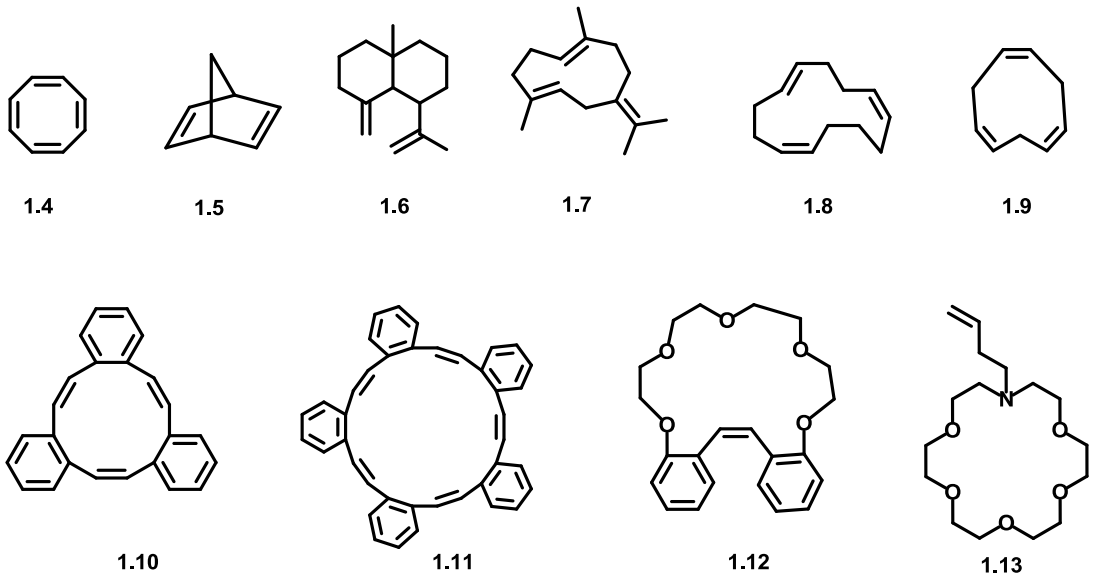


Figure 1.9 *– Olefin containing compounds that act as ligands for silver.*

The first X-ray crystal structure of a silver-alkene complex was reported by Mathews *et al.*[95] by reacting cyclooctatetraene (**1.4**) with silver nitrate. The two distal C=C bonds of **1.4** interact with silver in a chelating manner, as shown in Figure 1.10. Interestingly, one of the silver-alkene interactions is

stronger than the second one. Following this Baenziger *et al.* in 1966 reported the crystal structure of norbornadiene (**1.5**) with silver nitrate, in which the two C=C bonds interact with two silvers in a bridging manner.[96]

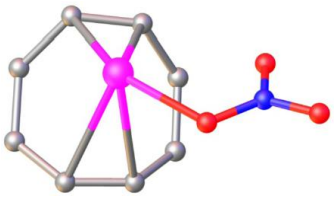


Figure 1.10 *– The first crystallographycally characterised silver-alkene complex.*[95] [56]

One of the driving forces for the x-ray crystal structure analysis of silver-olefin complexes is to determine the configuration and confirmations of non-crystalline hydrocarbons. These include natural products such as β-gorgonene (**1.6**)[97] and germacratriene (**1.7**),[98] and strained or unusual hydrocarbons such as cis,trans,cis-1,5,9-cyclotridecatriene (**1.8**)[99] and cis,cis,cis-1,4,7-cyclononatriene (**1.9**).[100] The complex with **1.8** showed the interaction of a single silver atom with the three C=C bonds but a complex with **1.9** formed a trinuclear adduct through the interaction of the three C=C bonds with three silver atoms, as shown in Figure 1.11.

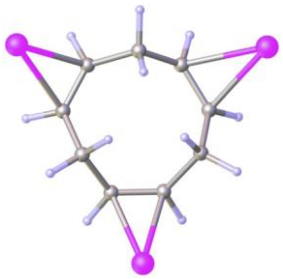
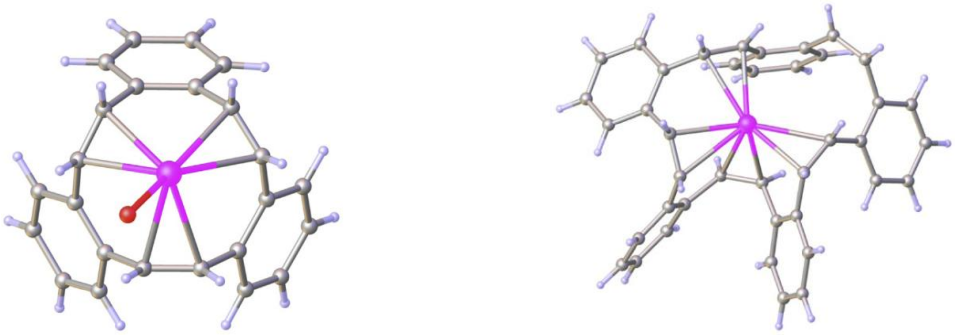


Figure 1.11 *– A trinuclear complex formed from ligand **1.9**.*[56]

In addition to the determination of the structure of the silver-β-gorgonene (**1.6**) complex, a silver-alkene interaction was utilised to purify **1.6** from other hydrocarbons.[97] This brings us to another important feature of silver-alkene interaction that has been utilised for some time. The use of the silver-alkene interactions for the separation of unsaturated hydrocarbons is an established practice with silver(I) nitrate the most commonly used reagent. Methods of

separation include impregnating silver(I) nitrate upon solid supports such as silica gel, alumina, amberlyst resin and Sephadex, HPLC and precipitating solid silver(I) complexes, with the target compound, out of a solution mixture. These methods can be applied to the separation of geometric and constitutional isomers that differ in the placement of olefinic groups, the separation of alkene-containing compounds and alkene impurities from alkanes.[56, 101-102]

Annulenes are another family of supramolecular host type molecules that form complexes with silver through the coordination of the olefin groups. Annulene **1.10** has a more rigid structure relative to **1.11** and formed a discrete assembly through the coordination of the three olefin groups with a single silver atom and the silver atom also interacted with the oxygen atom of the triflate counter anion, as shown in Figure 1.12A.[103] **1.11** is flexible relative to **1.10** so it can change its shape to suit the size of the silver complex. **1.11** gave a 1D polymeric assembly through the interaction of only one of the alkene functional groups of the annulene and the aromatic ring from the second ligand molecule. Silver also has an interaction with the oxygen atom of the triflate counter anion. However, with silver(I) perchlorate **1.11** gave a discrete assembly by coordinating through four of the alkene functional groups in a chelating manner, as shown in Figure 1.12B.[104] The interaction of four olefin groups with a single silver atom is very rare. The interesting feature of the two discrete assemblies of the silver-annulene complexes is the preference of the silver atom to form the silver-alkene interaction over the benzene rings.



A) B)

Figure 1.12 *– The structures of the complexes of annulenes* ***1.10*** *(A) and* ***1.11*** *(B). The oxygen atom of the triflate anion is shown in A.*[56, 103-104]

The silver(I)-alkene interaction has also been exploited for the determination of crystal structure of silver(I)-crown ether complexes.[105] By incorporating an alkene group, shown in Figure 1.9, into crown ethers silver(I) complexes of ligand **1.12** and **1.13** were reported. Crown ether **1.12** gave a discrete assembly with silver(I) nitrate through the interaction of only three oxygen atoms and the alkene functional group of **1.12**. The silver atom also coordinated with the nitrate anion. The interesting features of this structure are, the preferred interaction of the silver atom with the alkene functional group over the aromatic rings and the simultaneous interaction of the silver atom with “hard” oxygen atoms of the ether and a “soft” π-bond with the olefin group.[105] Similarly, the lariat ether (**1.13**) forms a discrete assembly with silver(I) nitrate. Silver chelates with the nitrogen atom and the olefin group of the butenyl arm of the crown ether, as shown in Figure 1.13.[106]

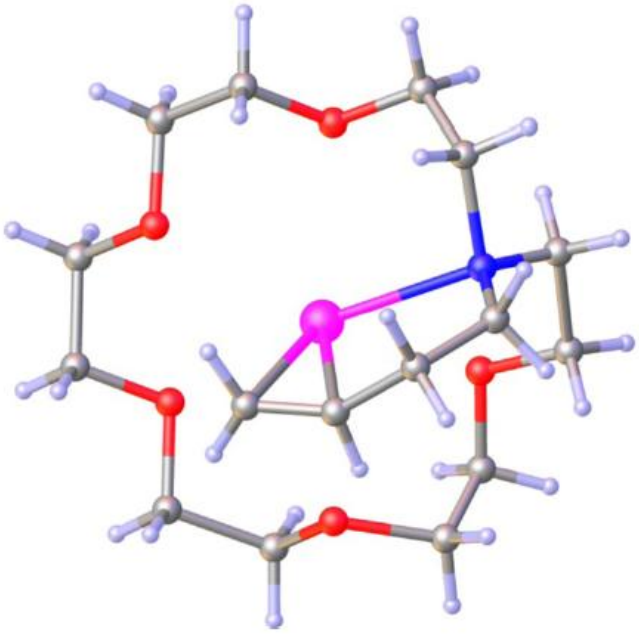
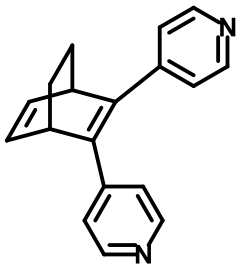


Figure 1.13 *– The discrete assembly of silver complex of lariat ether (**1.13**)*

1.6 Silver-alkene interactions in metallosupramolecular chemistry

The application of silver-alkene interaction in metallosupramolecular chemistry arose when Steel *et al.* observed a η^2-type silver-alkene interaction in their attempt to make a triangular assembly using ligand **1.14** and silver nitrate.[107]



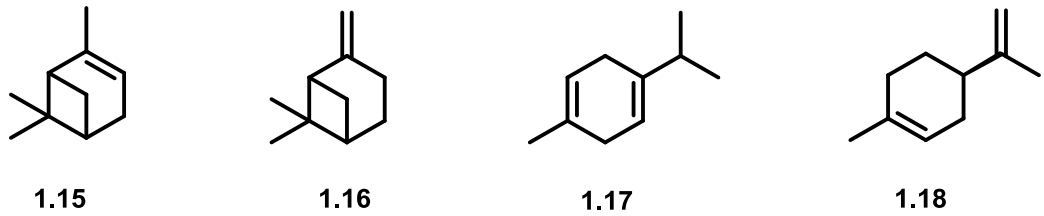
1.14

Figure 1.14 *– Ligand **1.14** designed to provide the 60° angle requirement for triangular assembly.[107]*

As shown in Figure 1.14, ligand **1.14** was designed to provide the 60° angle required for triangle formation and the silver in the form of silver nitrate as a linear linker through the interaction of the two pyridine nitrogen atoms of the

ligand; however, the silver atom coordinated not only to the pyridine nitrogen atoms but also to the more exposed double bond of the bicyclooctadiene unit of the ligand.

From this observation Steel *et al.* conclude that it is possible to construct metallosupramolecular assemblies by using solely alkene functional group containing ligands and different silver(I) salts. Following this, they reported discrete and 1D polymeric structures using different silver(I) salts and natural products **1.15**-**1.18** shown in Figure 1.15.[108]



1.15 **1.16** **1.17** **1.18**

Figure 1.15 *– Natural products used as metallosupramolecular synthons.[108]*

Ligand **1.15** and **1.16** gave discrete assemblies with silver(I) perchlorate and silver(I) hexafluorophosphate, respectively, in 1:2 (silver: ligand) ratio. Ligand **1.18**, similar to the silver complexes of **1.15** and **1.16** gave a discrete mononuclear assembly with silver(I) hexafluorophosphate. However, with silver(I) triflate **1.18** gave a 1D polymeric assembly by coordinating through the two alkene functional groups. Ligand **1.17** also gave a 1D polymeric assembly with silver(I) hexafluorophosphate, in which the alkene functional groups of the ligand bridges adjacent silver atoms.

Following the coordination chemistry of the above natural products with different silver(I) salts, Steel *et al.*[56, 60, 109] extended their work by using different ligands containing olefin group with a central aromatic core structure, as shown in Figure 1.16. The introduction of aromatic rings into the design of the ligand is advantageous since the aromatic rings can also interact with the silver and there is a possibility of π-π interaction between the aromatic rings, which increases the stability of the structure. The other advantage is the possibility of adding different types and numbers of olefin containing arms.

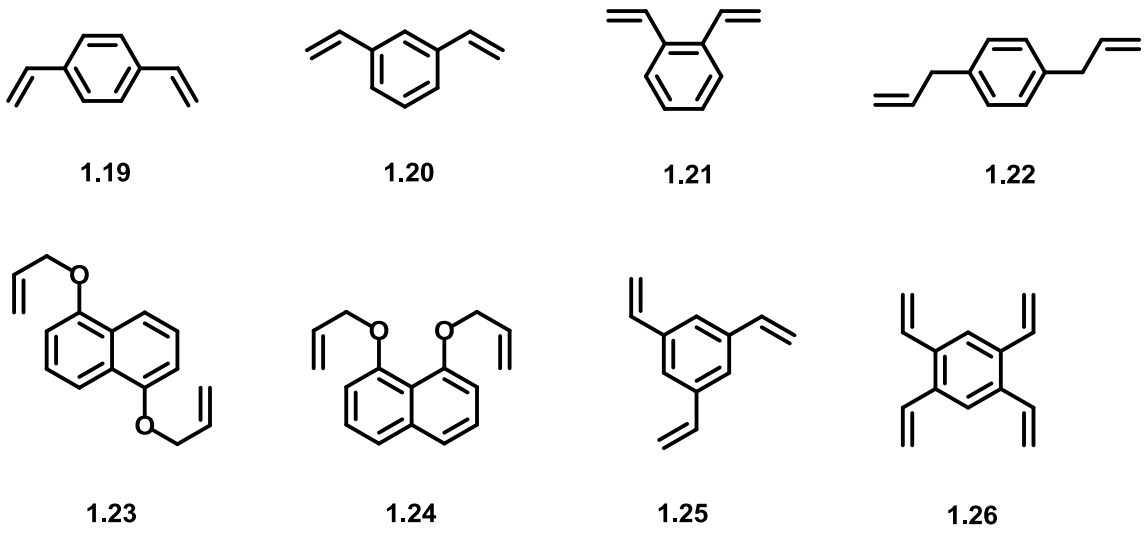
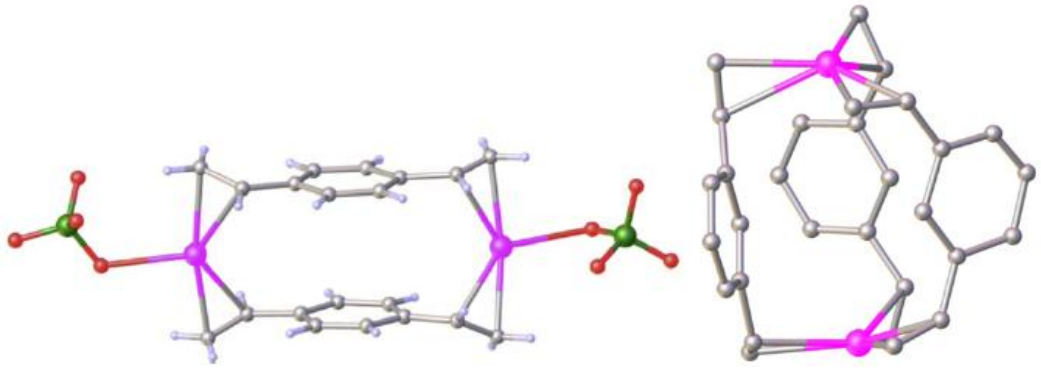
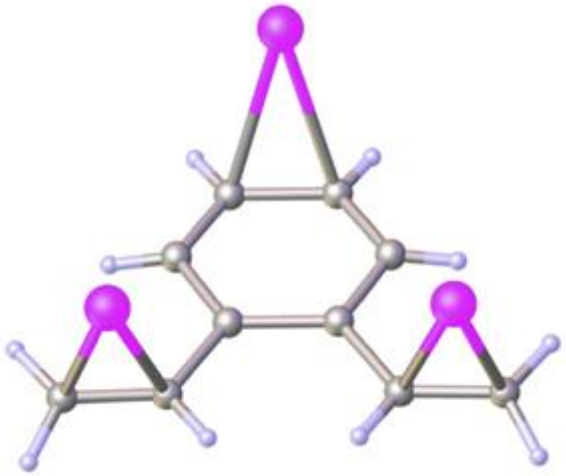


Figure 1.16 *– Ligand molecules used to investigate the silver-alkene interaction in metallosupramolecular chemistry.*

Ligand **1.19** gave a dimetallomacrocyclic structure with silver(I) perchlorate through the interaction of the vinyl group with silver, as shown in Figure 1.17A. Ligand **1.20** gave an M_2L_3 cage like structure with silver(I) tetrafluoroborate (Figure 1.17B), while a 1D polymeric assembly formed with silver(I) perchlorate. A 2D polymeric assembly was obtained from the reaction of ligand **1.21** with silver(I) perchlorate. In this complex, in addition to the vinyl arms of the ligand, the benzene ring also interacted with silver. Interestingly, all the silver ligand interactions are from the same face of the ligand, as shown in Figure 1.17C.[56, 109]



A) B)



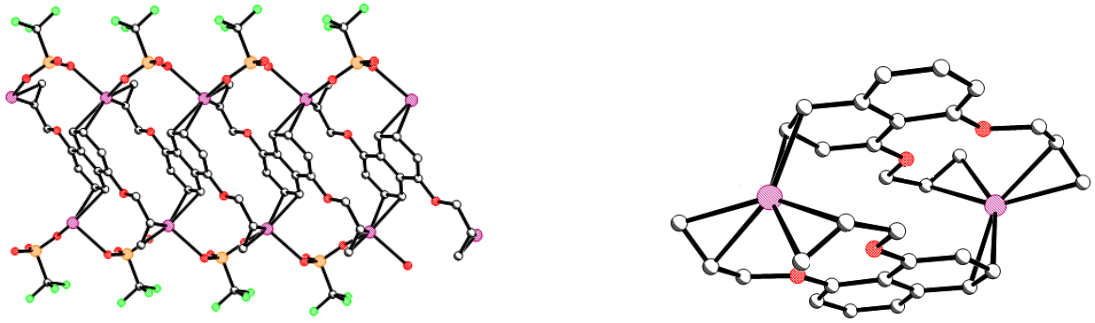
C)

Figure 1.17 *– The structures of complexes of silver(I) with ligands* ***1.19***-***1.21****. A) The discrete dimetallomacrocycle assembly of complex of silver(I) perchlorate with ligand* ***1.19****. B) The discrete* M_2L_3 *cage like structure of the complex of silver(I) tetrafluoroborate with ligand* ***1.20****. All hydrogen atoms and the counter anions have been omitted for clarity. C) Part of the 2D polymeric assembly of the complex of* ***1.21*** *with silver(I) perchlorate, showing the silver-ligand interaction from the same face of the ligand. The counter anions have been omitted for clarity.*[56, 109]

1,4-Diallylbenzene (**1.22**) contains an additional carbon atom spacer in the functional arms relative to 1,4-divinylbenzene (**1.19**). Ligand **1.22** gave 1D polymeric assembly with silver(I) perchlorate, while ligand **1.19** forms a discrete dimetallomacrocycle, as shown in Figure 1.17A.

This group took their investigation of ligands containing olefins as metallosupramolecular synthons further by changing the core structure from benzene to naphthalene, which gave them an opportunity not only to increase the number of isomers that could be attained, but increased the probability of having π-π interactions between the aromatic rings and η^2-type silver-arene interactions. For instance, 1,5-diallyloxynaphthalene (**1.23**) gave a 1D

necklace polymer with silver(I) triflate. As shown in Figure 1.18A, the ligand interacts with silver in a tetradentate manner by using the olefin groups of the allyloxy arms and the two aromatic rings of naphthalene in a η^2-fashion. 1,8-Diallyloxynaphthalene (**1.24**) gave a discrete [2+2] macrocyclic structure with silver(I) triflate. The allyloxy arms of the ligand chelates with silver, which is also coordinated with the naphthalene ring, as shown in Figure 1.18B.



A) B)

Figure 1.18 *– The structures of complexes of ligand* ***1.23*** *and* ***1.24*** *with silver(I) triflate.*[60] *A) Part of the 1D necklace polymeric assembly of the complex of* ***1.23*** *with silver(I) triflate. Hydrogen atoms have been omitted for clarity. B) The discrete [2+2] macrocyclic structure of the complex of* ***1.24*** *with silver(I) triflate. All hydrogen atoms and the triflate counter anion have been omitted for clarity.*

This study was further extended by using multiply armed ligands with benzene cores such as 1,3,5-trivinylbenzene (**1.25**) and 1,2,4,5-tetravinylbenzene (**1.26**). Ligand **1.25** gave a 1D polymeric assembly with silver(I) perchlorate, in which the ligand interacted with three silver atoms in a tridentate manner through the three vinyl arms. The reaction of ligand **1.26** with silver(I) tetrafluoroborate resulted in the formation of an interesting silver sandwich, in which two of the ligand molecules gather four silvers in a planar array, as shown in Figure 1.19.[56, 60]

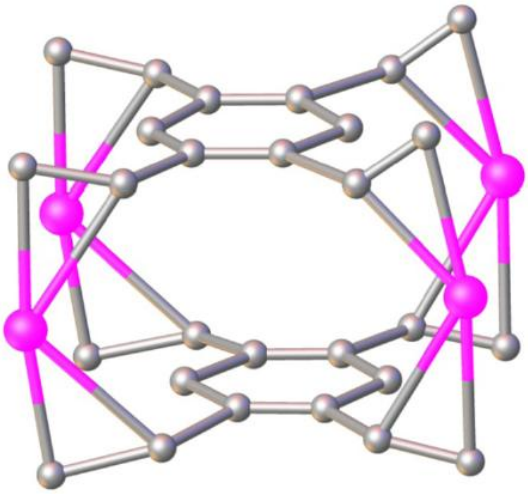


Figure 1.19 *– The silver sandwich formed from* ***1.26*** *and silver(I) tetrafluoroborate.*[56] [60]

In general, for silver(I)-alkene or silver(I)-arene interaction a range between 2.16 Å and 2.94 Å for Ag-C bond distances has been reported.[80, 110] Throughout this thesis the silver-alkene interaction to be considered as bonding, the individual Ag-C bond distances must be 2.65 Å or less and also the distance between silver and the centroid of the C=C bond is 2.55 Å or less. These distances are arbitrary and were chosen as they cover the vast majority of Ag-C distances within this work. This definition also applies to the η^2 coordination of aromatic systems. In the case of η^1 coordination the distance must be 2.65 Å or less between the silver atom and the carbon atom. The sum of the ionic radii of silver(I) and oxygen is 2.66 Å [110] and within this thesis, when the distance between silver and oxygen is 2.60 Å or less the silver-oxygen interactions are considered as bonding.

The silver-alkene interaction is considered as a two electron, three centred bond where two alkene carbons are considered to occupy one coordination site of the silver atom. The angle between the olefinic group and other coordinating species is measured from the centroid of the C=C bond. In most of these complexes, the geometry around the silver atom is not exact, for four coordinate complexes the parameter τ_4, introduced by Houser *et al.*,[111] is used. The τ_4 parameter is easily calculated using equation (1) and involves the

sum of the two largest angles in the four coordinate species, α and β, subtracted from 360 °, which is then divided by 141 °.

$$\tau_4 = \frac{360^o - (\alpha + \beta)}{141^o} \qquad (1)$$

The values of τ_4 range from 1.00 for a perfect tetrahedral geometry to 0 for a perfect square-planar geometry. The intermediate τ_4 values and their corresponding geometries are shown in Figure 1.20.

tetrahedral
T_d
$\theta_{1\text{-}6} = 109.5^o$

trigonal pyramidal
C_{3V}
$\theta_{1\text{-}3} = 120^o$
$\theta_{4\text{-}6} = 90^o$

Seesaw
C_{2v}
$\theta_1 = 180^o$
$\theta_{2\text{-}5} = 90^o$
$90 < \theta_6 < 180^o$

Square planar
D_{4h}
$\theta_{1\text{-}2} = 180^o$
$\theta_{3\text{-}6} = 90^o$

	τ_4
Tetrahedral (T_d)	1.00
Trigonal pyramidal (C_{3v})	0.85
Seesaw (C_{2v}, $\theta_6 = 90^o$)	0.64
Seesaw (C_{2v}, $\theta_6 = 109.5^o$)	0.50
Seesaw (C_{2v}, $\theta_6 = 154.4^o$)	0.18
Seesaw (C_{2v}, $\theta_6 = 170^o$)	0.07
Square planar (D_{4h})	0.00

Figure 1.20 *– Geometries and corresponding τ_4 values for four coordinate species.*[111]

For five coordinate complexes the parameter τ_5, introduced by Addison *et al.*[112] is used. The τ_5 parameter is easily calculated using equation (2) and involves the difference of the two largest bond angles in the five-coordinate complex to give an index of the degree of trigonality.

$$\tau_5 = \frac{\beta - \alpha}{60} \qquad (2)$$

Hence, a trigonal bipyramidal structure has a τ_5=1, while a square pyramidal structure has τ_5=0.[111-113]

There is much debate whether silver forms metal-metal bonds or not. Within metallic silver the Ag-Ag bond length is 2.884 Å[114] and the sum of two silver van der Waals radii is 3.44 Å.[114] Dance *et al.*[115] reported an Ag···Ag separation distance of 2.886(4) Å and described it as non-bonding by arguing that the Ag^+ bonding was fulfilled by two linearly coordinated thiolate ligands with a slight distortion from linearity as indication of weak repulsion not attraction. However, new theoretical and experimental evidence[116-117] showed that there is a significant Ag-Ag bond.[118]

1.7 Thesis coverage

The previous Steel group member, Jeni Burgess[60] showed the suitability of olefin containing ligands with silver as new synthons for metallosupramolecular chemistry. This project expands the previous work by using ligands containing allyloxy, diallylamine and allyl groups. Changing the core structures of the ligand as well as the number of alkene functional groups within a ligand are especially explored in this project.

Characterisations of ligands were performed by using ^{1}H NMR, ^{13}C NMR, mass spectrometry, infrared (IR) spectroscopy, elemental analysis, melting point and X-ray crystal structure analysis when applicable. The assignments of ^{1}H and ^{13}C NMR spectra for some of the ligand molecules were supported by 2D HSQC and HMBC spectra. Characterisations of complexes relied on single crystal X-ray structure determination and elemental analysis.

Chapter Two reports about complexes obtained from ligands containing allyloxy arms. The number of allyloxy arms varied from one to six and also incorporate different types of aromatic rings. Ligands containing one allyloxy arm use quinoline and azobenzene core structures, two allyloxy arm containing ligands use bisphenol moieties and the multi-allyloxy arm containing ligands use benzene and other types of spacer groups.

Chapter Three explores complexes of ligands containing diallylamine groups with different core structures such as benzene, pyridine, pyrimidine and triazine cores. The ligands are classified into three classes, depending on the number of diallylamine groups attached. The first class is ligands containing one diallylamine group with pyridine or pyrimidine core structures. The second class of ligands are those containing two diallylamine groups with benzene, biphenyl, pyrimidine and triazine core structures. The third class of ligands are those containing three diallylamine groups with benzene, pyrimidine and triazine core structures. These classes of ligands, containing diallylamine groups, were used to investigate the Ag-σ-donor interaction with the nitrogen atom of the heterocyclic ring and Ag-π-donor coordination with the alkene functional group.

Chapter Four discusses complexes of ligands containing allyl arms. Most of the ligands used in this chapter are urea based, which gives us an opportunity to investigate the contribution of the carbonyl oxygen atom of the urea moiety in the assembly of the complex. It also contains a ligand that has a silicon atom as a core.

Chapter Two

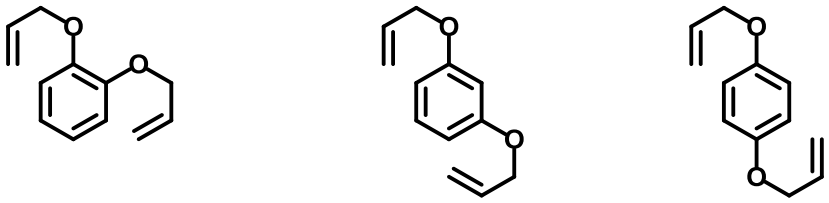
Complexes of ligands containing allyloxy groups

Chapter Two

Complexes of ligands containing allyloxy groups

2.1 Introduction

The use of ligands containing allyloxy arm as synthons for metallosupramolecular assembly with different silver(I) salts is not a new concept. Previously, the Steel group used ligands containing allyloxy arm with benzene and naphthalene cores to construct different assemblies.[60] Helical, 1D and 2D polymeric assemblies were prepared, by using the ligands shown in Figure 2.1 with different silver(I) salts.



(2.1) **(2.2)** **(2.3)**

Figure 2.1 *– Ligands containing allyloxy group with benzene core structures previously used by the Steel group in the construction of different assemblies.[60]*

Ligand **2.1** was reacted with silver(I) perchlorate, hexafluorophosphate and triflate that gave 1D helical assemblies. In all cases, the ligand bridges neighbouring silver atoms through the allyloxy arms.

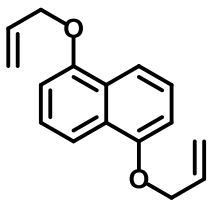
1,3-Diallyloxybenzene (**2.2**) was reacted with silver(I) hexafluorosilicate to give a 2D polymeric assembly. There are two crystallographically independent silver atoms in this structure, which are bridged by the ligand through η^2-type coordination. In addition to the η^2-type coordination of the olefin group, the benzene ring has η^1-type coordination with one of the silver atoms.

This work was also extended using 1,4-diallyloxybenzene (**2.3**) with silver(I) perchlorate and tetrafluoroborate.[56, 60] The complex with silver(I) perchlorate gave a 1D polymeric assembly by bridging adjacent silver atoms through the olefins. Unlike the perchlorate complex, the silver(I) tetrafluoroborate complex

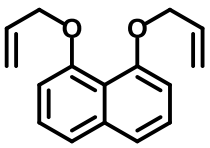
with **2.3** gave a 2D polymeric assembly through the interaction of the alkene functional groups of the allyloxy arm and η^2-type coordination of the benzene ring.[60]

Interestingly, this investigation of ligands containing allyloxy group, with benzene core structures as synthons of metallosupramolecular chemistry, is limited to ligands **2.1**-**2.3**; however, there has been an in depth investigation of the ligands containing allyloxy group with naphthalene core structures.

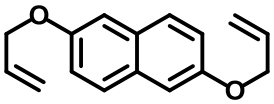
The advantages of using the naphthalene core structure over benzene are numerous; firstly an increased number of disubstituted isomers relative to only three (ortho, meta and para) in benzene, secondly an increase in the separation distance between the coordinating sites and finally increased possibility of having symmetrical ligands. Symmetry consideration is one of the recommended suggestions in designing ligands for metallosupramolecular synthons.[26, 119] Moreover, naphthalene is a larger aromatic system, which has greater potential for η^2-arene-silver(I) coordination to occur as any electron cloud perturbation introduced by the coordination of silver(I) can more effectively be spread over a two ring system than a one ring system.[120] Considering the above advantages over the benzene core structure, the Steel group designed symmetrical diallyloxy ligands with naphthalene core structures, some of which are shown in the following Figure.[60]



(2.4)



(2.5)



(2.6)

Figure 2.2 *– some of the diallyloxy ligands with naphthalene core used by the Steel group in the construction of different metallosupramolecular assemblies.*[60]

Ligand **2.4** acts as a tetradentate ligand through the coordination of both allyloxy arms and the arene ring with silver(I) triflate. There are two η^2-type

coordinations of the naphthalene ring with silver, both of which are at the expected positions in terms of resonance consideration.[121] The overall structure is a 1D necklace polymer in which **2.4** bridges four silver atoms.

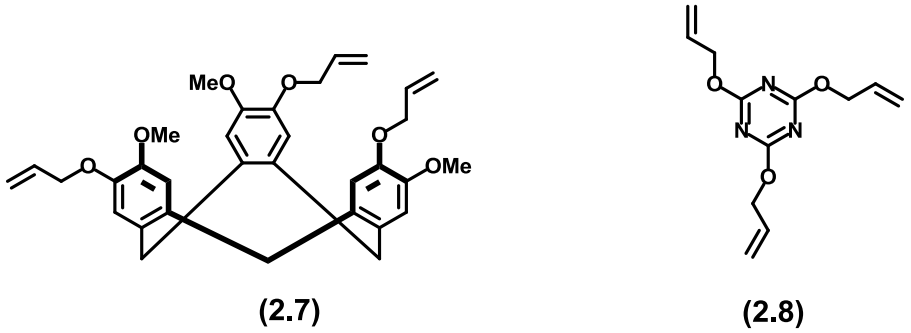
Ligand **2.5** was used to construct a [2+2] macrocycle with silver(I) triflate through the chelation of the allyloxy arms and η^2-type coordination of the arene ring with silver. This structure is the first chelation type assembly of the ligands containing allyloxy group with a naphthalene core structure. A similar structure was obtained with silver(I) perchlorate.

A 2D polymeric assembly was obtained with ligand **2.6** and silver(I) tetrafluoroborate. Similar to ligand **2.5**, ligand **2.6** was coordinated with silver through the allyloxy arms and the arene ring of the central naphthalene.[56, 60]

In general, the Steel group showed different assemblies from discrete to 2D polymeric structures using ligands containing allyloxy group with naphthalene cores.

In related work, Hardie's group extended their work on cyclotriveratrylene-based ligands[122] to the tris-allyloxy derivative (**2.7**), which produced interesting network structures and one discrete complex upon reaction with various silver(I) salts.[56, 123]

In my BSc. Honours project, a 1D polymeric assembly was obtained from ligand **2.8** and silver(I) perchlorate. In this structure, all the allyloxy arms and the central triazine ring nitrogen atoms are coordinated with silver.[124] Ligand **2.8** also gave a cluster with copper(I) chloride by using all the three allyloxy arms and one nitrogen atom from the central triazine ring for coordination.[125]



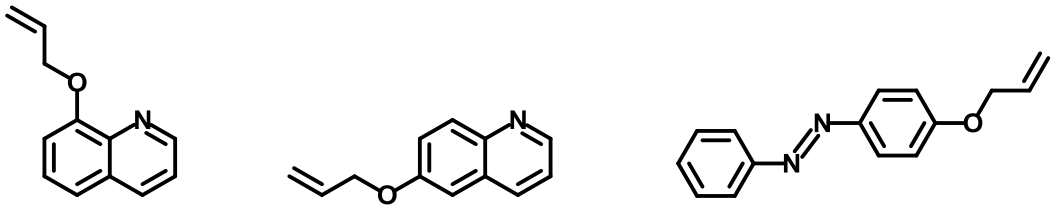
(2.7) **(2.8)**

Figure 2.3 *– The tris-allyloxy derivative of a cyclotrivertrylene-based ligand (**2.7**) and 2,4,6-triallyloxy-1,3,5-triazine ligand (**2.8**) used previously in the construction of different metallosupramolecular assemblies.*

From these observations, we found this area of chemistry to be under exploited and we designed this project to extend the study further, by using ligands with different numbers of allyloxy arms. This chapter describes the coordination chemistry of the ligands containing allyloxy group with different silver(I) salts. Depending on the number of allyloxy groups in the ligand, they are classified into four major classes.

2.2 Ligands containing one allyloxy group

The coordination of ligands containing one allyloxy arm with different silver(I) salts has been investigated using the quinoline and azobenzene based ligands shown in Figure 2.4.

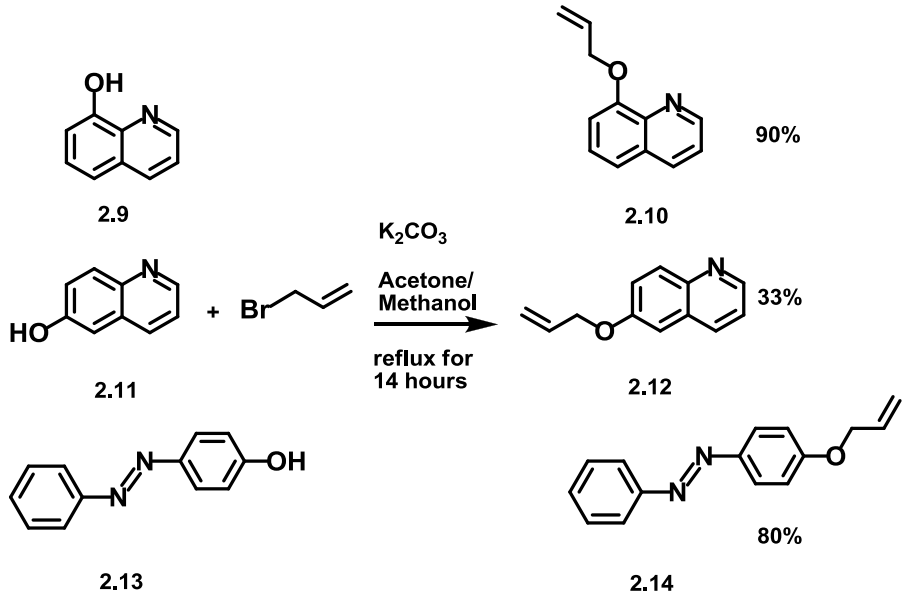


2.10 **2.12** **2.14**

Figure 2.4 *– Ligands containing one allyloxy group.*

2.2.1 Synthesis of ligands containing one allyloxy arm

Ligands **2.10, 2.12** and **2.14** were synthesised from their corresponding hydroxyl functional groups using the following scheme.



Scheme 2.1 - Synthesis of ligands **2.10**, **2.12**, and **2.14** from their corresponding hydroxyl precursors.

All these compounds are known compounds, **2.10**[126] as a precursor in the study of photoluminescence of tris-(7-substituted-8-hydroxyquinoline)aluminium complexes, **2.12**[127] as a precursor for the synthesis of pyridyl-fused 3-amino chroman derivatives and **2.14**[128-129] to develop photo-tunable chromatography.

*2.2.2 Complex of 8-allyloxyquinoline (**2.10**)*

<u>With silver(I) perchlorate(**2.15**)</u>

Ligand **2.10** was reacted with two equivalents of silver(I) perchlorate in acetone. Slow diffusion of diethyl ether into the reaction mixture yielded golden crystals suitable for X-ray crystal structure analysis. The structure was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains one full ligand, one silver atom and a non-coordinated perchlorate anion, revealing a 1:1 (metal:ligand) ratio complex or M_1L_1 type coordination complex, as shown in Figure 2.5.

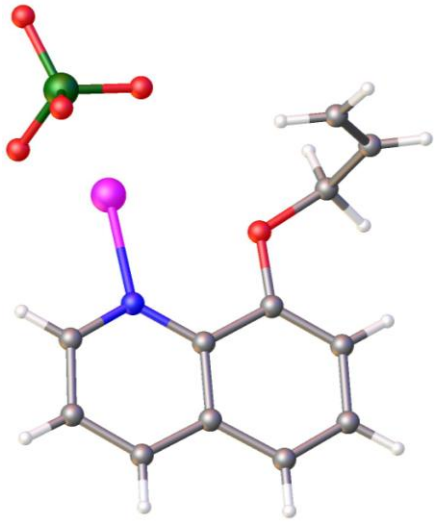


Figure 2.5 *– The asymmetric unit of complex* ***2.15****.*

The structure grows into a 1D polymeric assembly through the coordination of the olefin group and the nitrogen atom of the quinoline ring. There is no chelation of the allyloxy arm and the quinoline nitrogen atom of the same ligand with a single silver atom; instead the silver atom bridges a quinoline nitrogen atom of the first ligand with the allyloxy arm of the next ligand. The quinoline ring alternates its position, which keeps the coordination sites of the ligand in the right place for a bridging mode of coordination, as shown in Figure 2.6.

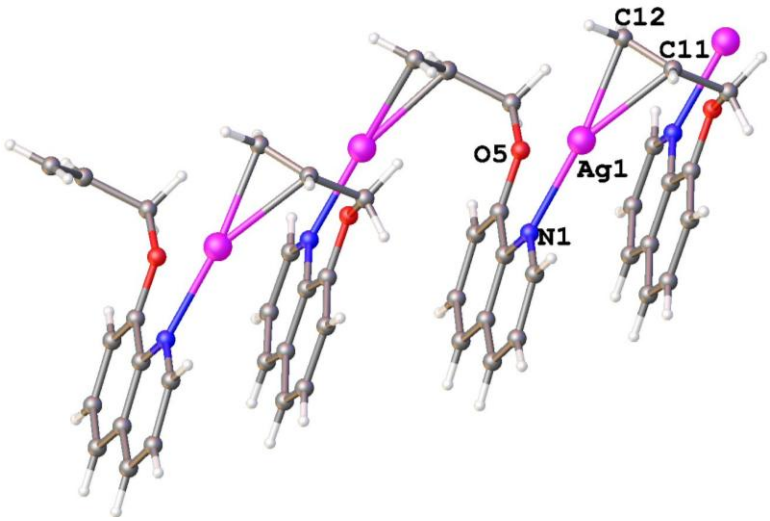


Figure 2.6 *– Part of the 1D polymeric assembly of complex* ***2.15****. The non-coordinated perchlorate anion has been omitted*

for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.219(2), Ag1-C11 2.416(3), Ag1-C12 2.296(3), Ag1-C11,C12 2.264(3), N1-Ag1-C11 157.1(1), N1-Ag1-C12 166.7(1), N1-Ag1-C11,C12 170.2(1).

The silver-quinoline nitrogen atom bond length (2.219 Å) is similar to the related silver-pyridine nitrogen complexes, in which the silver(I) atom is two coordinate.[130-132] The bond distance between silver and the centroid of the olefin group (Ag1-C11,C12) as well as with the individual carbon atoms (Ag1-C11 and Ag1-C12) are in the expected bond length range for η^2-type coordination of silver with olefins.[60, 110, 133] The silver atom is two coordinate with a nitrogen atom from the quinoline ring and one alkene functional group. The bond angle measured between the centroid of the olefin group and the nitrogen atom of quinoline (N1-Ag1-C11,C12) is 170.2°. The measured bond angle indicates the presence of a slightly bent assembly from the ideal linear 180.0°; this may arise from a weak interaction of the allyloxy oxygen (O5) with silver (Ag1-O5 2.627 Å). This bond distance is shorter than the sum of the ionic radii between silver(I) and oxygen, which is 2.66 Å.[60, 110] Considering the position of the ethereal oxygen atom of the allyloxy arm, which is suitable for the formation of a stable five membered chelate ring with silver and the short distance measured between Ag1 and O5, the twist of the two coordinate silver from the ideal linear structure is not surprising. The shortest separation distance between the oxygen atom of the perchlorate anion and silver atom is 2.742 Å, which is too long for silver-oxygen distance to be considered as an interaction. The separation distance between the centroids of adjacent quinoline rings is 4.322 Å. This long separation distance may be the result of the long allyloxy arm coordination with silver, which separates the adjacent quinoline rings and removes any potential for a π-π interaction. Ligand **2.10** bridges symmetry related adjacent silver atoms through the coordination of the olefin group and the nitrogen atom of quinoline with a separation distance of 5.479 Å.

*2.2.3 Complex of 6-allyloxyquinoline (**2.12**)*

With silver(I) triflate (**2.16**)

Ligand **2.12** was mixed with two equivalents of a solution of silver(I) triflate in acetone. Diethyl ether diffusion into the reaction mixture resulted in the growth of crystals suitable for X-ray crystal structure analysis. The structure was solved in the triclinic P-1 space group. The asymmetric unit contains two full ligand molecules, two silver atoms and two coordinating triflate counter anions, as shown in Figure 2.7.

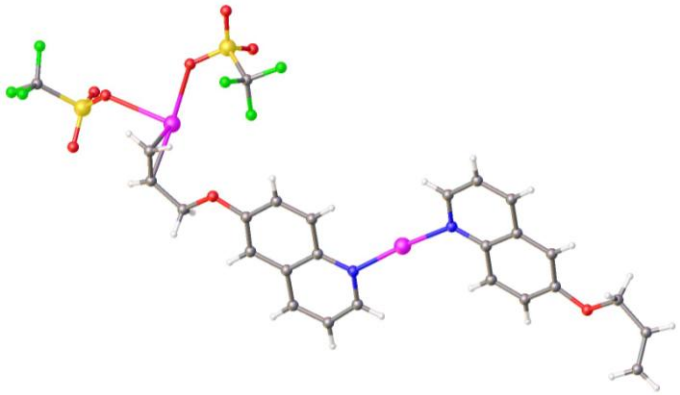
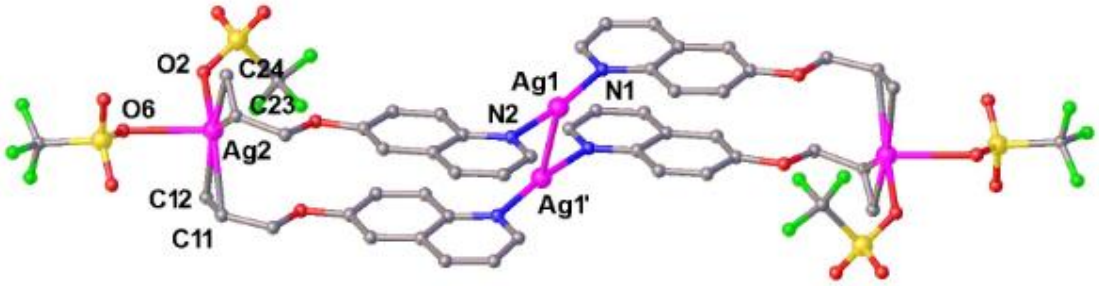


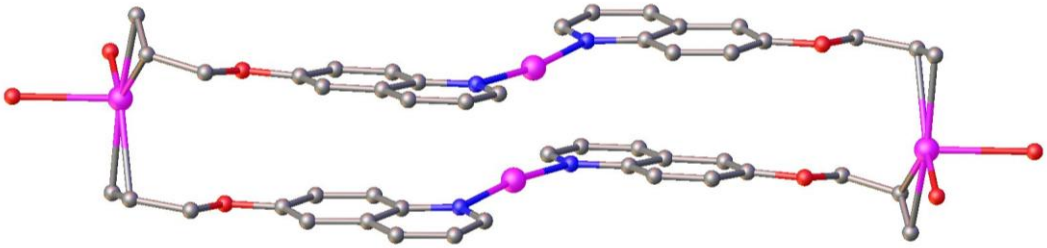
***Figure 2.7** – The asymmetric unit of complex **2.16**, showing the coordination of two ligand molecules through the quinoline nitrogen atom and the olefin with two silver atoms. One of the silver atoms also coordinates with triflate anions.*

The overall structure of complex **2.16** is a tetranuclear discrete assembly that involves the coordination of four silver atoms and four ligand molecules to produce a [4+4] macrocycle or an M_4L_4 coordination complex, as shown in Figure 2.8. There are two crystallographically independent silver atoms that have different coordination numbers. Ag1 bridges adjacent ligands through the interaction of silver-quinoline nitrogen atoms with a silver-nitrogen bond length (Ag1-N1) of 2.139 Å, which is similar to the silver-nitrogen bond length in complex **2.15**. Ag1 has also a long range interaction with the symmetrically equivalent silver atom Ag1' with (Ag1-Ag1') separation distance of 3.368 Å, which is shorter than the sum of two silver van der Waals radii 3.44 Å[114, 134] but longer than the separation of silver atoms in silver metal 2.884 Å[114, 135-136]

as well as other silver-silver contacts reported in the literature.[115, 137] Due to this long separation distance, the Ag1-Ag1' interaction is weak. The measured bond angle in N1-Ag1-N2 is 172.9°, which is not the linear 180°. This might be attributed to the weak Ag1-Ag1' interaction. The structure without the Ag1-Ag1' interaction is shown in Figure 2.8B.



A)



B)

Figure 2.8 *– The [4+4] discrete assembly of complex* ***2.16****. A) Showing the full structure of the complex with the long Ag1-Ag1' interaction. B) Showing the discrete assembly of the [4+4] complex by omitting the long Ag1-Ag1' interaction. All hydrogen atoms and part of the triflate anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.136(3), Ag1-N2 2.141(3), Ag1-Ag1' 3.368(2), N1-Ag1-N2 172.9(1), Ag2-C11 2.420(4), Ag2-C12 2.373(4), Ag2-C11,C12 2.302(4), Ag2-O2 2.333(3), Ag2-O6 2.544(3), Ag2-C23 2.469(4), Ag2-C24 2.344(4), Ag2-C23,C24 2.315(4), C11-Ag2-O2 128.6(1), C12-Ag2-O2 97.2(1), C11,C12-Ag2-O2 113.1(1), C11-Ag2-O6 96.1(1), C12-Ag2-O6 87.8(1), C11,C12-Ag2-O6 92.1(1), C11-*

Ag2-C23 103.5(2), C11-Ag2-C24 135.1(2), C12-Ag2-C23 135.7(2), C12-Ag2-C24 167.3(2), C11,C12-Ag2-C23,C24 134.8(2), O6-Ag2-C23 100.9(1), O6-Ag2-C24 96.2(1), O6-Ag2-C23,C24 99.0(1).

The individual carbon-silver and also the centroid of olefin to silver (C11,C12-Ag2-C23,C24) bond lengths are in the expected range for η^2-type silver-olefin interactions.[60, 110, 133] The bond length measured for Ag2-O2 is 2.333 Å, which is shorter than the bond length measured for Ag2-O6, 2.544 Å; however, both are in the expected range for silver-oxygen interactions.

Ag2 is four coordinate with two olefins of the ligand and two triflate counter anions. The largest bond angle around the environment of Ag2 is measured between the centroids of the olefins (C11,C12-Ag2-C23,C24) with a bond angle of 134.8° and the second largest bond angle is between O2 and the centroid of C11=C12, 113.1°. The calculated τ_4 value for Ag2 is 0.80, revealing a trigonal pyramidal geometry. Ligand **2.12** acts as a bidentate bridging ligand to give a separation distance of 9.580 Å between the two symmetrically independent silver atoms (Ag1 and Ag2).

The tetranuclear discrete assembly is further stabilized by a close π-π interaction between the quinoline rings. The separation distance measured between the centroid of the two rings is 3.660 Å, which is longer than the value in graphite (3.350 Å)[130] but shorter than the separation distances measured in a series of copper and cobalt complexes of tetrakis(2-imidazolinyl)benzene, which have separation distances between 3.9 to 4.4 Å.[15-16, 138]

The structure of complex **2.16** can be described as a rectangular assembly. The two quinoline rings coordinated with silver through the nitrogen atom makes the long side of the rectangle, while the silver coordinated with the olefin provides the shorter side of the rectangle. This kind of rectangular structure has been observed in the literature using two ferrocene-bridged bis(pyridines) with silver(I) perchlorate.[27, 139]

*2.2.4 Complexes of 4-allyloxyazobenzene (**2.14**)*

With silver(I) perchlorate (**2.17**)

Ligand **2.14** was reacted with two equivalents of silver(I) perchlorate in acetone. Diethyl ether diffusion into the reaction mixture afforded crystals suitable for X-ray structure analysis. The structure solved in the triclinic P-1 space group. The asymmetric unit contains one full ligand molecule, one silver atom and a disordered perchlorate anion, revealing a 1:1 (metal:ligand) ratio complex, as shown in Figure 2.9.

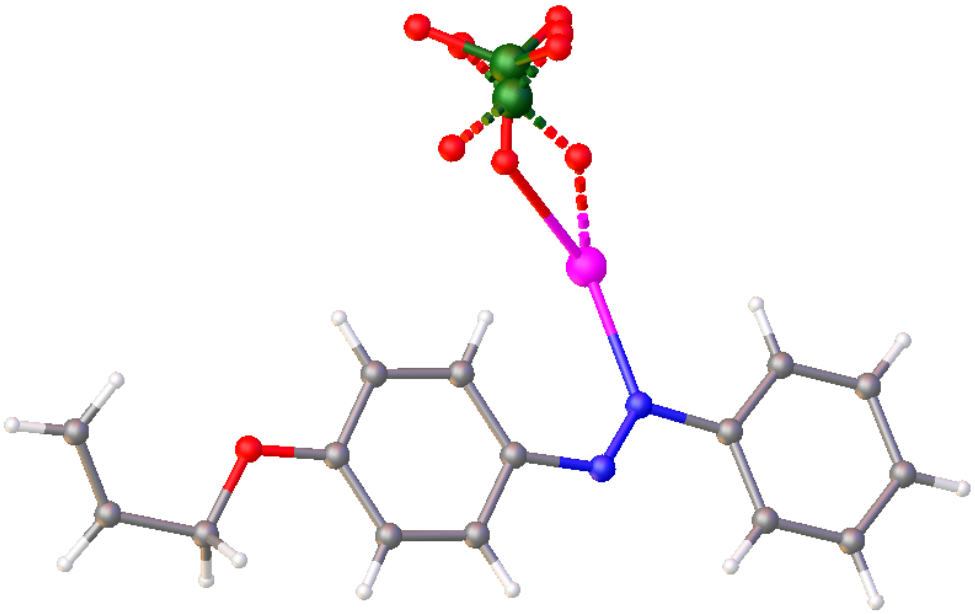


***Figure 2.9** – The asymmetric unit of complex **2.17** showing the coordination of silver with one of the azo-nitrogen atoms. The disordered perchlorate anion is represented in broken bonds.*

The perchlorate anion is disordered over two positions with 85% dominant position occupancy. The overall structure of complex **2.17** is a discrete [2+2] macrocycle with a rectangular shape, as shown in Figure 2.10.

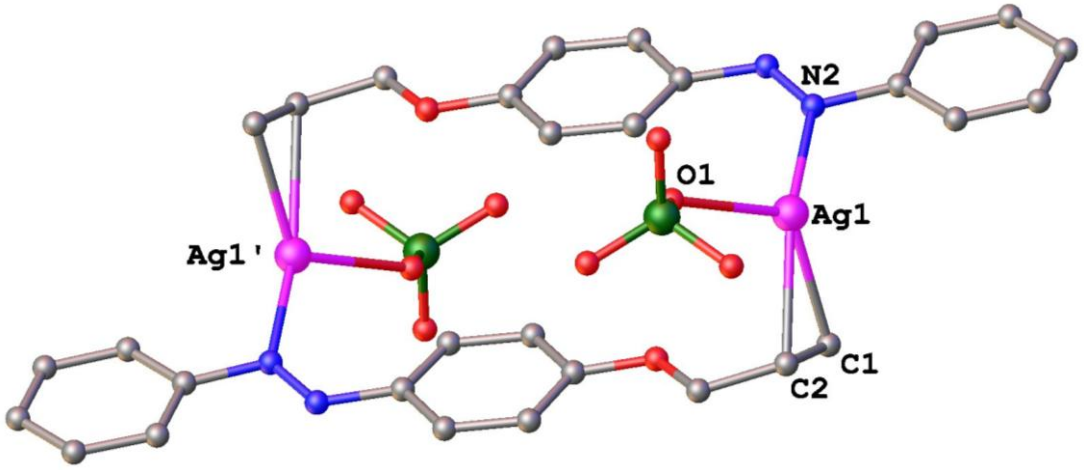


Figure 2.10 *– The discrete [2+2] macrocycle of complex* ***2.17****. All hydrogen atoms and the disordered perchlorate anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N2 2.286(3), Ag1-O1 2.500(3), Ag1-C1 2.350(4), Ag1-C2 2.437(3), Ag1-C1,C2 2.297(4), N2-Ag1-O1 117.7(1), N2-Ag1-C1 114.2(1), N2-Ag1-C2 145.9(1), N2-Ag1-C1,C2 130.4(1),O1-Ag1-C1 120.1(1), O1-Ag1-C2 89.3(1), O1-Ag1-C1,C2 104.5(1).*

The silver atom is three coordinate through the coordination of one allyloxy arm of the ligand, one nitrogen atom of the azo group and an oxygen atom of the perchlorate anion. The largest bond angle around the silver environment is measured between the azo nitrogen atom and the centroid of the olefin group (N2-Ag1-C1,C2) with a bond angle of 130.4°. The two other bond angles are N2-Ag1-O1 (117.7°) and O1-Ag1-C1,C2 (104.5°). The measured bond angles are distorted relative to the 120.0° angle for three coordinate trigonal shaped structures. The bond distance measured between silver and the nitrogen atom is similar to the silver-azo nitrogen bond distances measured in the literature.[140] The bond length measured for silver-oxygen as well as the silver carbon distances are in the expected range for such types of interactions.

Interestingly, the interaction of the allyloxy arm and the azo nitrogen atom with silver is directional. The trans position of the azobenzene rings and the directional interaction of the ligand are the reasons for the formation of a rectangular shaped structure, in which the longer side of the rectangle is

formed by the bridging ligand, while the shorter sides are formed by the bridging silver atoms. The longer side of the rectangle is measured between Ag1····Ag1' with a separation distance of 8.765 Å and the shorter side is measured between the coordinated azo nitrogen atom and the centroid of the olefin group with a separation distance of 4.162 Å.

The directional interaction of the ligand offsets the aromatic rings, which minimizes any possibility of π-π interactions between the benzene rings. The two perchlorate anions coordinate with silver from opposite directions, which minimizes any steric interaction.

With silver(I) nitrate (**2.18**)

Ligand **2.14** was reacted with two equivalents of silver(I) nitrate in water. Slow evaporation of the solvent over two weeks afforded crystals suitable for X-ray crystal structure analysis. The structure of complex **2.18** was solved in the triclinic P-1 space group. The asymmetric unit contains one full ligand molecule, one silver atom and a coordinated nitrate anion, revealing a 1:1 (metal:ligand) ratio complex, as shown in Figure 2.11.

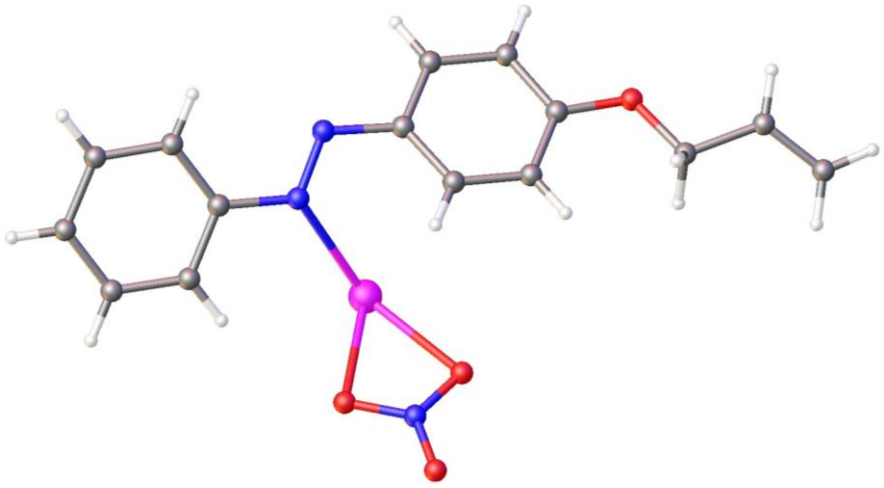


Figure 2.11 *– The asymmetric unit of complex* ***2.18****.*

The overall structure of complex **2.18** is a discrete [2+2] macrocycle with a parallelogram structure, which is quite similar to complex **2.17**, as shown in Figure 2.12. The nitrate anion chelates with silver, which makes this structure different from complex **2.17**. The silver atom is four coordinate through the

coordination of the olefin, the azo nitrogen atom and two oxygen atoms from the nitrate counter anion.

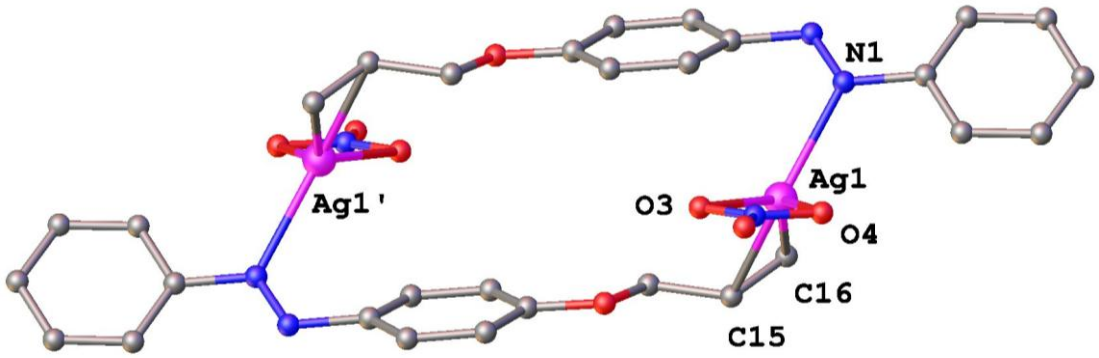


Figure 2.12 *– The [2+2] macrocycle of complex* ***2.18****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.380(1), Ag1-O3 2.461(2), Ag1-O4 2.456(2), Ag1-C15 2.407(2), Ag1-C16 2.318(2), Ag1-C15,C16 2.266(2), N1-Ag1-O3 120.5(1), N1-Ag1-O4 99.5(1), N1-Ag1-C15 128.5(2), N1-Ag1-C16 97.7(2), N1-Ag1-C15,C16 113.5(2), O3-Ag1-O4 52.3(1), O3-Ag1-C15 104.8(2), O3-Ag1-C16 137.6(2), O3-Ag1-C15,C16 120.9(2), O4-Ag1-C15 128.7(2), O4-Ag1-C16 143.6(2), O4-Ag1-C15,C16 138.1(2).*

The largest bond angle around the environment of the silver atom is measured between one of the coordinated oxygen atoms of the nitrate anion and the centroid of the coordinated olefin group (O4-Ag1-C15,C16) with the measured bond angle of 138.1°. The second largest bond angle (O3-Ag1-C15,C16) is 120.9° and the third largest angle (N1-Ag1-O3) is 120.5°. From these measured bond angles the calculated τ_4 value for silver is 0.72, which reveals a seesaw geometry.

The silver-nitrogen bond distance (2.380 Å) measured in complex **2.18** is longer than the silver-nitrogen bond distance (2.286 Å) measured in complex **2.17**. All the silver-oxygen interactions as well as the centroid of the olefin groups with silver are in the expected range for their respective type of interactions with silver. The longer side of the parallelogram structure of complex **2.18** is between Ag1 and Ag1’ with a separation distance of 8.436 Å

and the shorter distance is measured between the centroid of the olefin group (C15=C16) and N1 with a separation distance of 3.887 Å. These measured distances are shorter than the corresponding distances measured in complex **2.17**.

Generally, the trans positions of the benzene rings in the azobenzene and the directional interaction of the allyloxy arm towards the azo nitrogen atom are similar to complex **2.17**.

With silver(I) tetrafluoroborate (**2.19**)

Ligand **2.14** was also reacted with silver(I) tetrafluoroborate in the same manner as the previous complexes. Complex **2.19** is similar to the previous complexes and crystallizes in the triclinic P-1 space group. The asymmetric unit contains one ligand molecule, one silver atom and a non-coordinated tetrafluoroborate anion, revealing a 1:1 (ligand:metal) ratio, as shown in Figure 2.13.

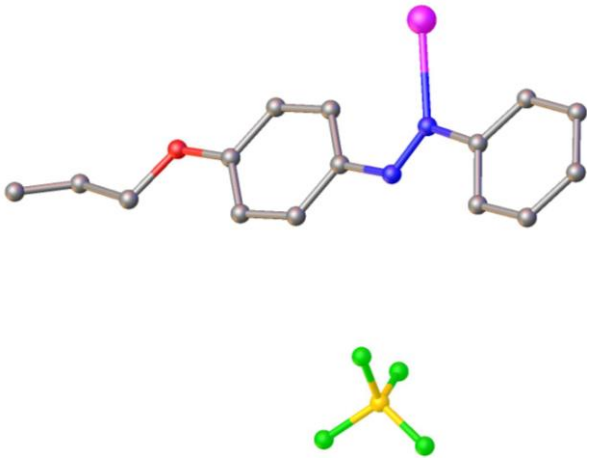


Figure 2.13 *– The asymmetric unit of complex* ***2.19****. All hydrogen atoms have been omitted for clarity.*

The overall structure is a discrete [2+2] macrocycle with a rectangular shape involving the coordination of the olefin group of the allyloxy arm and the azo nitrogen, as shown in Figure 2.14. One of the differences of complex **2.19** from **2.17** and **2.18** is the absence of coordination of the counter anion with silver, which makes silver a two coordinate bridging metal atom. The bond

angle measured between the centroid of the coordinated olefin group and the azo nitrogen (N1-Ag1-C1,C2) is 162.4°, which is far from the ideal linear bond angle of 180°. Relative to the largest bond angles measured in complexes **2.17** and **2.18**, 130.4° and 138.1° respectively, the bond angle measured around the environment of Ag1 in complex **2.19** (162.4°) is much closer to linear.

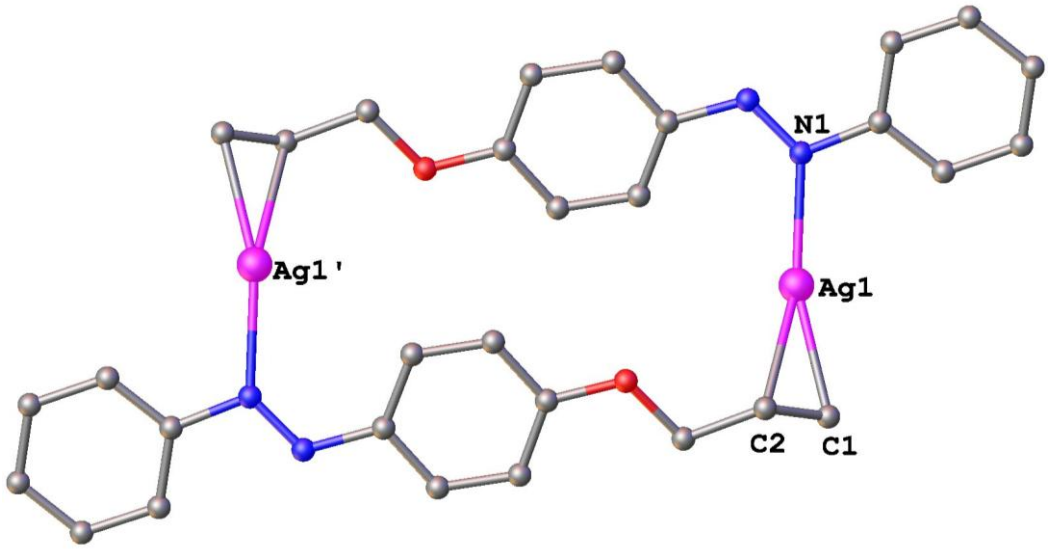


Figure 2.14 *– The discrete [2+2] macrocyle assembly of complex* ***2.19****. All hydrogen atoms and the non-coordinated tetrafluoroborate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.204(1), Ag1-C1 2.350(2), Ag1-C2 2.356(2), Ag1-C1,C2 2.256(2), N1-Ag1-C1 155.3(2), N1-Ag1-C2 156.6(2), N1-Ag1-C1,C2 162.4(2).*

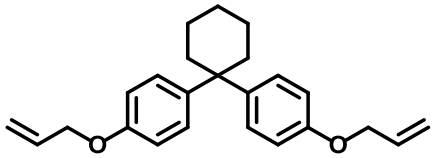
The silver-nitrogen bond length measured in this structure is shorter than the measured distances in complexes **2.17** and **2.18** as well as elsewhere in the literature.[140-141] Even though the counter anion is changed from coordinating to non-coordinating type, the general rectangular shape observed in complexes **2.17** and **2.18** did not change. The separation distance measured between Ag1 and Ag1' is 9.125 Å, which is longer than the Ag1···Ag1' separation distances measured in the corresponding complexes **2.17** and **2.18** (8.765 Å and 8.436 Å, respectively). The separation distance measured between the centroid of the coordinated olefin group and the azo nitrogen

(N1·····C1,C2) is 4.406 Å, which is longer than the separation distance measured in complexes **2.17** (4.162 Å) and **2.18** (3.887 Å). Similar to complexes **2.17** and **2.18**, the longer side of the rectangle is formed from the bridging ligand, while the shorter side is formed from the bridging silver atom.

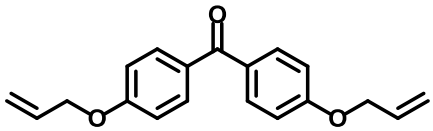
Generally, the coordination of the ligand with the silver atom is directional irrespective of the change in the solvent as well as the counter anion.

2.3 Ligands containing two allyloxy groups

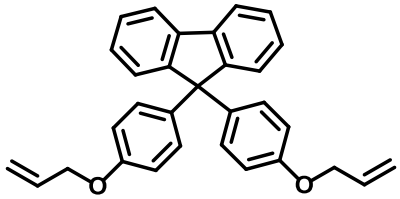
Complexes of ligands containing two allyloxy groups with different silver(I) salts were investigated using the following ligand molecules.



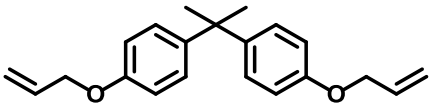
2.20



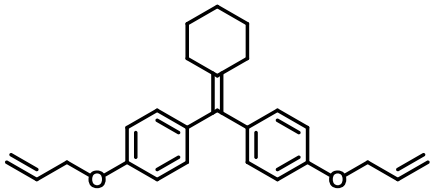
2.21



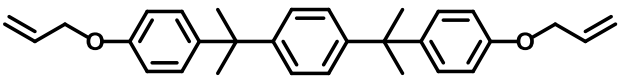
2.26



2.27



2.31



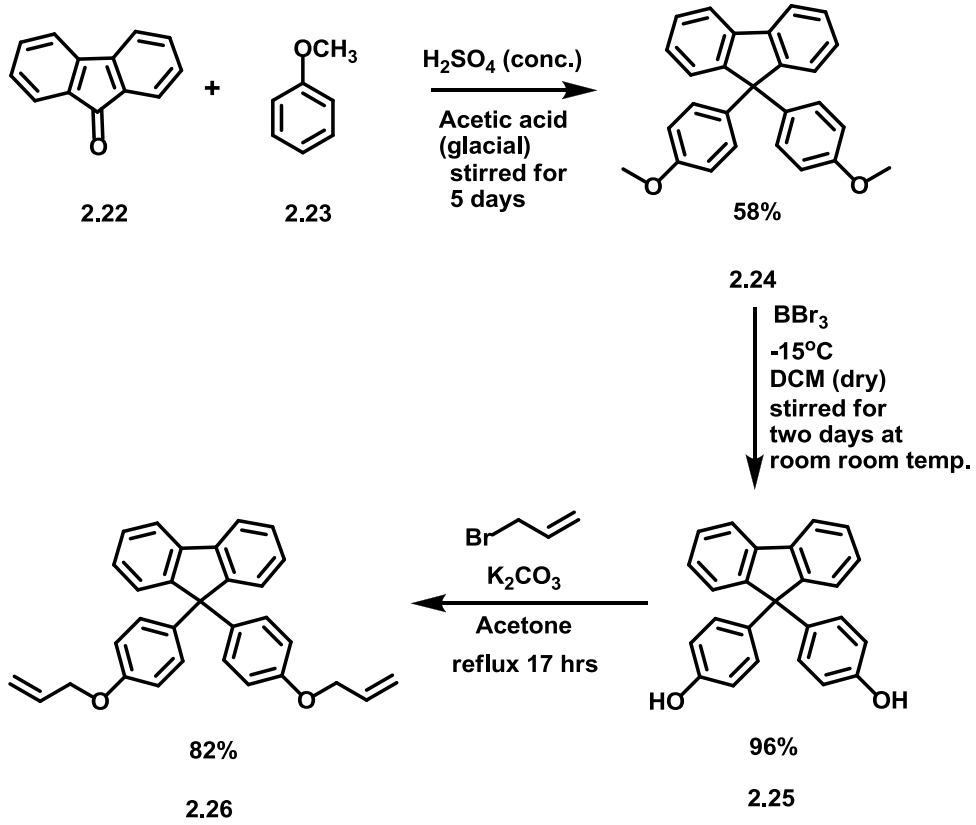
2.32

Figure 2.15 *– Ligands used to investigate the coordination of different silver(I) salts with ligands containing two allyloxy groups.*

2.3.1 Synthesis of ligands containing two allyloxy groups

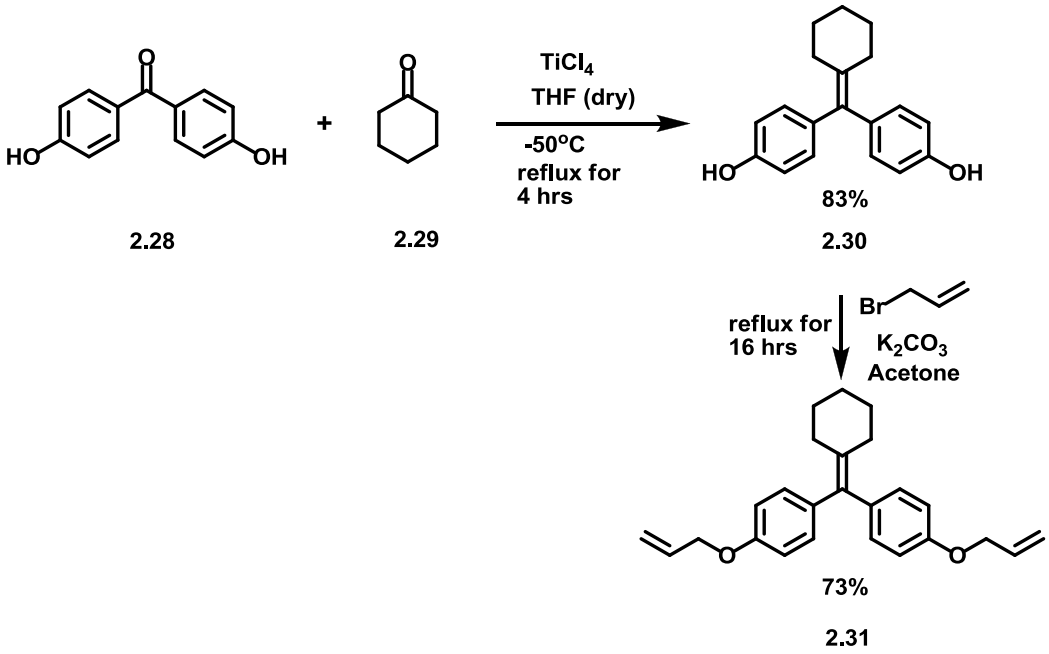
Ligands **2.20**, **2.21**, **2.27** and **2.32** were synthesised from their corresponding hydroxyl groups using the literature procedure,[142] shown in scheme 2.1. **2.20**,[143] **2.21**,[144] **2.27**,[145] **2.32**[143] are known compounds for various applications.

Ligand **2.26**[146] is a known compound and was synthesised by combinations of different literature methods[142, 147] in three steps, as shown in scheme 2.2.



Scheme 2.2 *– Synthesis of ligand* ***2.26****.*

Ligand **2.31** is also a known compound and was synthesised in two steps using combinations of adapted literature methods,[142, 148] as shown in scheme 2.3.



Scheme 2.3 *– Synthesis of ligand* ***2.31****.*

*2.3.2 Attempts to grow crystals of complexes of diallylether of bisphenol Z (**2.20**)*

Several attempts were made to grow crystals of different silver(I) complexes of ligand **2.20** using different crystal growing methods, from diethyl ether diffusion into the reaction mixture to using U and H-tubes, but none of them were successful.

*2.3.3 Complexes of 4,4'-di(allyloxy)benzophenone (**2.21**)*

With silver(I) perchlorate (**2.33**)

A solution of ligand **2.21** in a mixture of benzene and toluene was mixed with a solution of silver(I) perchlorate in acetone. Diethyl ether diffusion into the reaction mixture followed by slow evaporation of the solvent resulted in the growth of crystals suitable for single crystal structure analysis. The structure was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains one full ligand molecule, one silver atom and a coordinated perchlorate anion revealing a 1:1 (ligand:metal) ratio or an M_1L_1 type coordination complex, as shown in Figure 2.16.

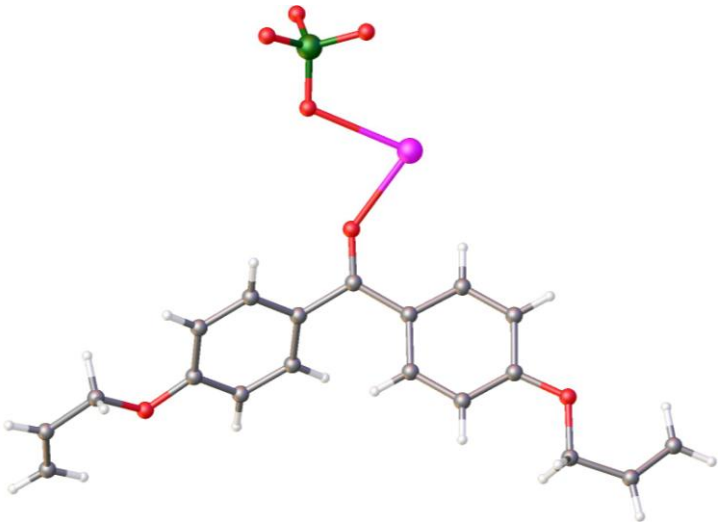


Figure 2.16 *– The asymmetric unit of complex* ***2.33****.*

The overall structure of complex **2.33** is a 2D polymeric assembly through the interaction of the carbonyl oxygen atom, the two olefins and the perchlorate anion with silver, as shown in Figure 2.17. The silver atom is four coordinate. The largest bond angle around the silver environment is measured between the centroids of the two olefins (C1,C2-Ag1-C18,C19, 129.2°). The calculated τ_4 value for silver is 0.76, revealing a seesaw geometry. As shown in Figure 2.17, the ligand acts in a tridentate manner using the carbonyl oxygen atom and the two alkene functional groups. The involvement of the carbonyl oxygen atom in the interaction of ligand **2.21** with silver offsets the aromatic rings and, therefore, no π-π interaction is observed in the structure of complex **2.33**.

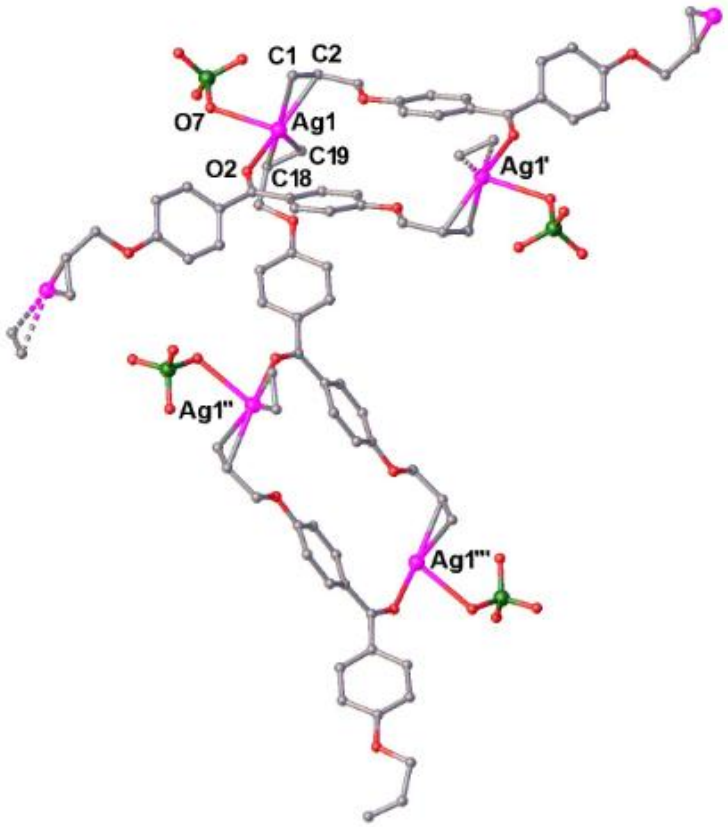


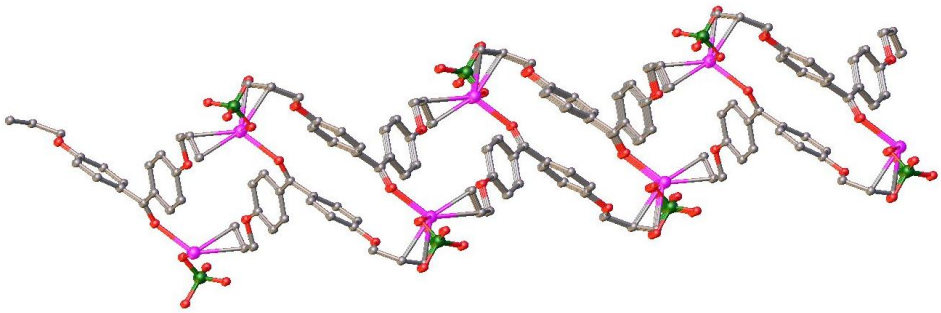
Figure 2.17 *– Part of the 2D polymeric assembly of complex* ***2.33****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O2 2.307(2), Ag1-O7 2.590(2), Ag1-C1 2.364(3), Ag1-C2 2.436(3), Ag1-C1,C2 2.304(3), Ag1-C18 2.486(3), Ag1-C19 2.420(3), Ag1-C18,C19 2.361(3), O2-Ag1-O7 79.5(2), O2-Ag1-C1 108.7(2), O2-Ag1-C2 137.8(2), O2-Ag1-C1,C2 123.8(2), O2-Ag1-C18 94.0(2), O2-Ag1-C19 118.9(2), O2-Ag1-C18,C19 106.5(2), O7-Ag1-C1 90.9(2), O7-Ag1-C2 108.7(2), O7-Ag1-C1,C2 99.8(2), O7-Ag1-C18 84.0(2),O7-Ag1-C19 106.7(2), O7-Ag1-C18,C19 95.3(2), C1-Ag1-C18 155.4(1), C2-Ag1-C18 127.6(1), C1-Ag1-C19 131.3(1), C2-Ag1-C19 99.1(1), C1,C2-Ag1-C18,C19 129.2(1).*

The silver-oxygen bond length measured between the silver atom and carbonyl oxygen (Ag1-O2, 2.307 Å) is shorter than the silver atom and the perchlorate counter anion (Ag1-O7, 2.590 Å). Both bond lengths are shorter than the sum of the ionic radii between silver(I) and oxygen (2.66 Å).[110] All

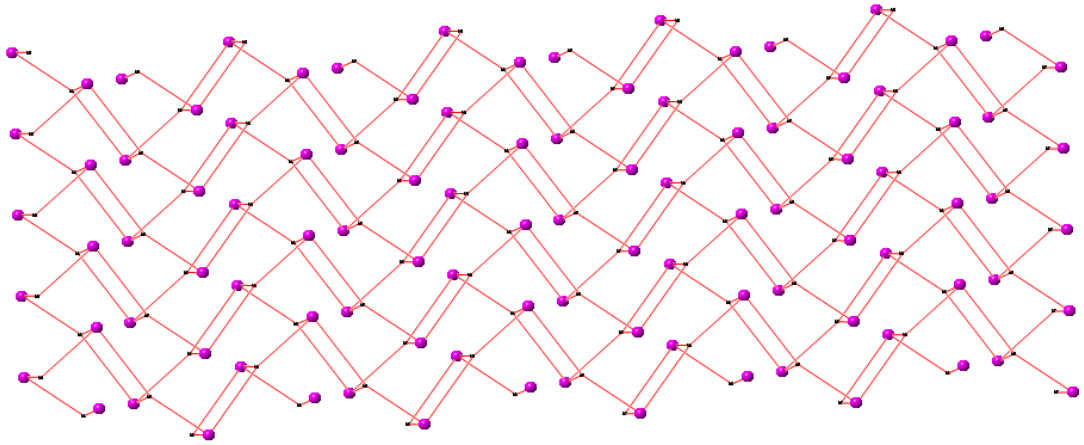
the measured silver-carbon bond distances are in the expected range for such types of interactions.

As shown in Figure 2.17, Ag1 and Ag1' are doubly bridged by the ligand through the carbonyl oxygen atom and the olefin group with an Ag1···Ag1' separation distance of 9.704 Å. This interaction results in a rectangular shaped assembly, with the longer side of the rectangle formed from half of the ligand due to the interaction of the carbonyl oxygen atom and the olefin group in a bridging manner, while the shorter side is formed from the bridging silver(I) atoms (Ag1 and Ag1'). Two of these rectangular shaped assemblies are bridged by another half of the ligand molecule through the interaction of the olefin group and the carbonyl oxygen with silver atoms. This interaction bridges Ag1 and Ag1" with a separation distance of 10.738 Å, as shown in Figure 2.17. Ligand **2.21** also bridges Ag1 and Ag1'" by interacting through the two olefin groups of the allyloxy arms with a separation distance of 16.266 Å.

Each ligand is connected to three silver atoms and each silver atom is also connected to three ligands; therefore, both the ligand and the silver atom are taken as the nodes of the 2D network system of complex **2.33**. The 2D topology of complex **2.33**, shown in Figure 2.18, can be represented as a 4.8^2 network, in which each node has one four and two eight membered ring circuits.



A)



B)

Figure 2.18 *– A) Side view of the 2D polymeric assembly of complex* ***2.33****. B) The network topology representation of complex* ***2.33****. All the pink balls represent the silver atoms, while the small black spots represent the ligand.*

From the side view of complex **2.33**, in Figure 2.18A, the ligands at the top layer of the polymer face down, while ligands from the bottom layer face upwards which puts the carbonyl oxygen atom from the bottom layer in close proximity to silver atoms coordinated with the olefins in the top layer and vice versa.

<u>With silver(I) hexafluorosilicate (**2.34**)</u>

The formation of complex **2.34** was serendipitous, since the original solution contained a mixture of ligand **2.21** and silver(I) tetrafluoroborate in xylene/acetone mixture. Slow evaporation of the solvent over two weeks resulted in the decomposition of the tetrafluoroborate anion to form HF. The HF reacted with the glass of the reaction vial to form silver(I) hexafluorosilicate. Single crystal X-ray diffraction was performed and the structure solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains one full ligand molecule, two silver atoms, three water molecules and one hexafluorosilicate anion, as shown in Figure 2.19.

As shown in Figure 2.20, the overall structure of complex **2.34** is a 1D zigzag polymeric structure, in which the ligand bridges adjacent silver atoms through

the olefin groups. Ligand **2.21** interacts in a linear bidentate mode to link adjacent silver atoms (Ag1····Ag2') with a separation distance of 15.277 Å. Unlike complex **2.33**, the ligand interacts only through the olefin groups; no interaction of the carbonyl oxygen atom of the ligand was observed.

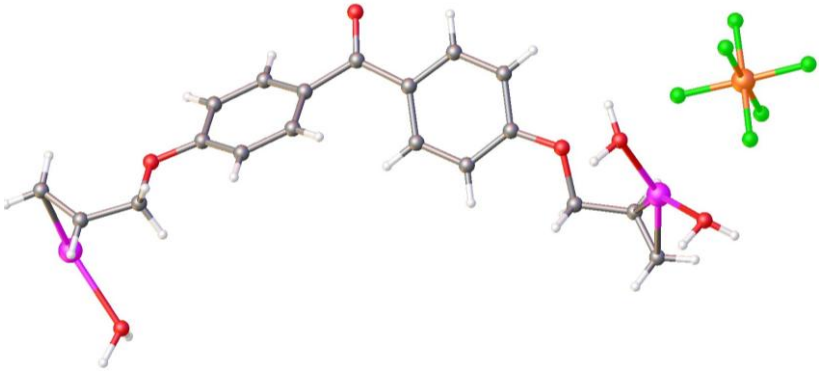


Figure 2.19 *– The asymmetric unit of complex* ***2.34****.*

Each silver atom coordinates with only one alkene functional group unlike the observation in complex **2.33**. The two crystallographically independent silver atoms (Ag1 and Ag2) have different coordination numbers. Ag1 is four coordinate, from the interactions of one olefin group, two bridging and one terminal water molecule. Ag2 is three coordinate from one alkene functional group and two bridging water molecules, as shown in Figure 2.20.

Ag1 and Ag2 are doubly bridged by two water molecules with Ag····Ag separation distance of 3.789 Å. The third water molecule coordinates with Ag1 as a terminal ligand.

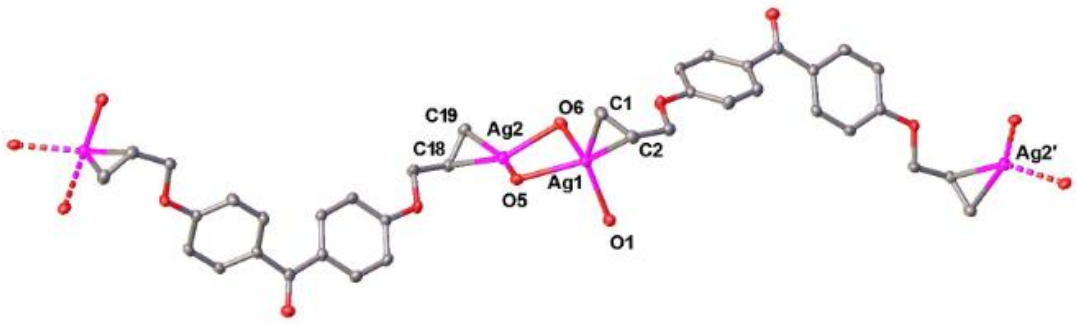


Figure 2.20 *– Part of the 1D zigzag polymeric assembly of complex* ***2.34****. All hydrogen atoms, non-coordinated hexafluorosilicate anions are omitted for clarity. Selected bond*

lengths (Å) and angles (°): Ag1-O1 2.276(2), Ag1-C1 2.318(2), Ag1-C2 2.341(2), Ag1-C1,C2 2.231(2), Ag1-O5 2.466(2), Ag1-O6 2.447(2), O1-Ag1-C1 137.1(2), O1-Ag1-C2 104.3(2), O1-Ag1-C1,C2 120.6(2), C1-Ag1-O5 120.1(2), C2-Ag1-O5 146.9 (2), C1,C2-Ag1-O5 134.4 (2), C1-Ag1-O6 104.7(1), C2-Ag1-O6 124.6(1), C1,C2-Ag1-O6 115.5(1), O5-Ag1-O6 71.3(2). Ag2-C18 2.337(2), Ag2-C19 2.312(3), Ag2-C18,C19 2.227(3), Ag2-O5 2.322(2), Ag2-O6 2.361(1), C18-Ag2-O5 132.5(2), C19-Ag2-O5 154.8(2), C18,C19-Ag2-O5 145.6(2), C18-Ag2-O6 150.5(2), C19-Ag2-O6 117.4(2), C18,C19-Ag2-O6 134.0(2), O5-Ag2-O6 75.4(2).

The largest bond angle around the environment of Ag1 (134.4°) is measured between the centroid of C1=C2 and one of the oxygen atoms (O5) of the bridging water molecules. The other two large bond angles measured around Ag1 are (O1-Ag1-C1,C2 120.6°) and (O6-Ag1-C1,C2 115.4°). The calculated τ_4 value for Ag1 is 0.74, revealing seesaw geometry. The silver-oxygen bond length measured between the silver atom and the terminally bonded water molecule (Ag1-O1 2.276 Å) is shorter than the silver-oxygen bond measured between the silver atom and the bridging water molecules (Ag1-O5 2.466 Å) and (Ag1-O6 2.447 Å). The longer bond lengths measured for both Ag1-O5 and Ag1-O6 compared to Ag1-O1 may be explained by the bridging interaction of O5 and O6. In both cases, the silver-oxygen bond distance is shorter than the sum of the ionic radii measured between silver(I) and oxygen.[110]

The largest bond angle measured around Ag2 (145.6°) is between the oxygen atom of one of the bridging water molecules (O5) and the centroid of C18=C19. The other two bond angles (O6-Ag2-C18,C19 134.0°) and (O5-Ag2-O6 75°), reveals a highly distorted trigonal shape for Ag2. The bond lengths measured between Ag2 and the bridging oxygen atoms (Ag2-O5 2.322 Å and Ag2-O6 2.360 Å) are shorter than the bond lengths measured in between Ag1 and the corresponding oxygen atoms. The distance measured between the centroid of the coordinated olefin group and Ag2 (Ag2-C18,C19

2.227 Å) is shorter than the corresponding distance measured between the centroid of the olefin group coordinated with Ag1 (Ag1-C1,C2 2.231 Å).

The counter anion plays a significant role in the transformation of the 1D to 2D polymeric assembly through interlayer hydrogen bonding between the water molecules and fluorine atoms, as shown in Figure 2.21.

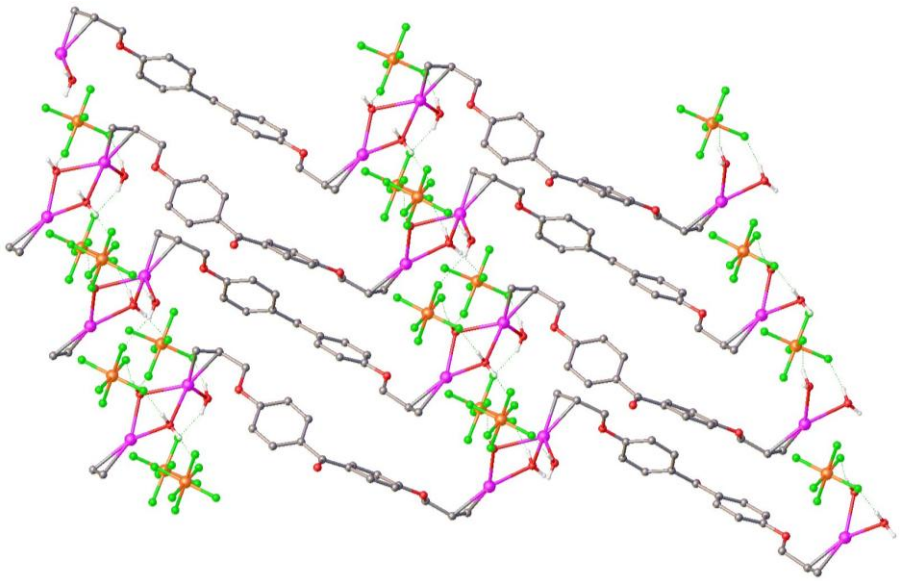


Figure 2.21 *– 2D polymeric assembly of complex* ***2.34*** *through interlayer hydrogen bonding interactions between water and hexafluorosilicate counter anions. All hydrogen atoms except for the water molecules are omitted for clarity.*

D-H····A	D-H	H····A	D····A	D-H····A
O-H····F	0.886	1.787	2.663	164.986

Table 2.1 *Hydrogen bonding geometry between the water molecules and the hexafluorosilicate counter anion.*

Evidence for the central atom in the counter anion being silicon not phosphorus was confirmed by the presence of six fluorine atoms and also improved refinement values. Moreover, there is only one counter anion per two silver(I) atoms which is consistent with a 2^- charge. The presence of the 2^-

charge and the Si-F bond lengths measured range between 1.662(2) - 1.700(2) Å, which are longer than the expected P-F bond lengths, which are between 1.565(4) – 1.621(1) Å.[60]

2.3.4 Complex of 9,9'-bis(4-allyloxyphenyl)fluorene (2.26)

With silver(I) perchlorate (**2.35**)

Ligand **2.26** was reacted with silver(I) perchlorate solution in nitromethane. Diethyl ether diffusion into the reaction mixture afforded crystals suitable for single crystal structure analysis. The structure of the complex solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand molecule, one silver atom and a coordinated perchlorate anion, revealing a 1:1 (metal:ligand) ratio or M_1L_1 type coordination complex.

As shown in Figure 2.22, the structure of the complex has disorder at one of the allyloxy arms of the ligand over two sites with dominant position occupancy of 80%. There is also a positional disorder at the perchlorate anion. When the perchlorate anion is not at a close range for coordination, a water molecule interacts with the silver atom. The dominant position occupancy for the perchlorate anion is also 80%.

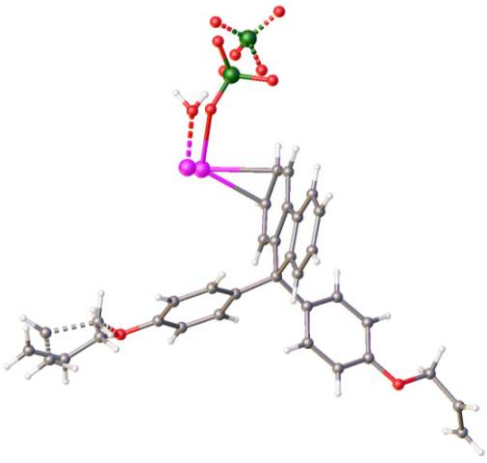
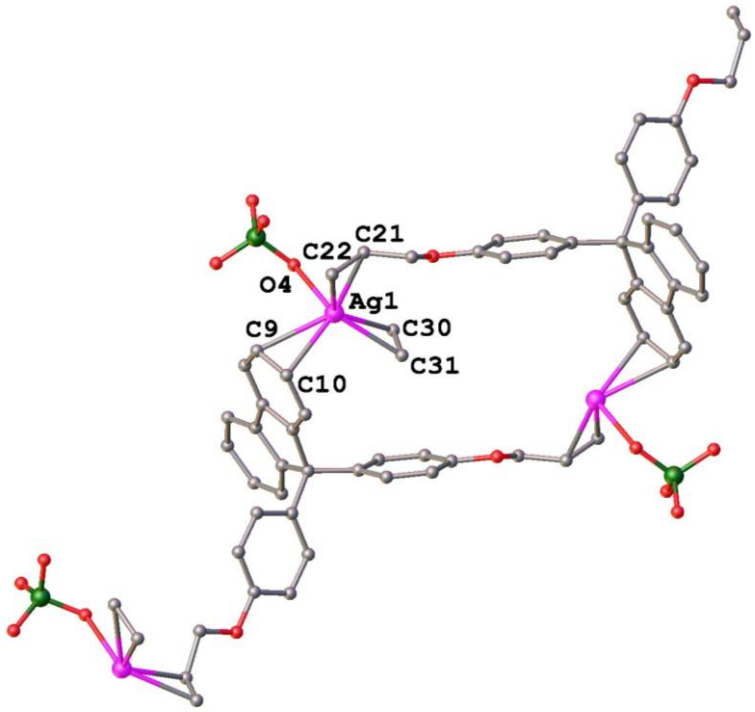
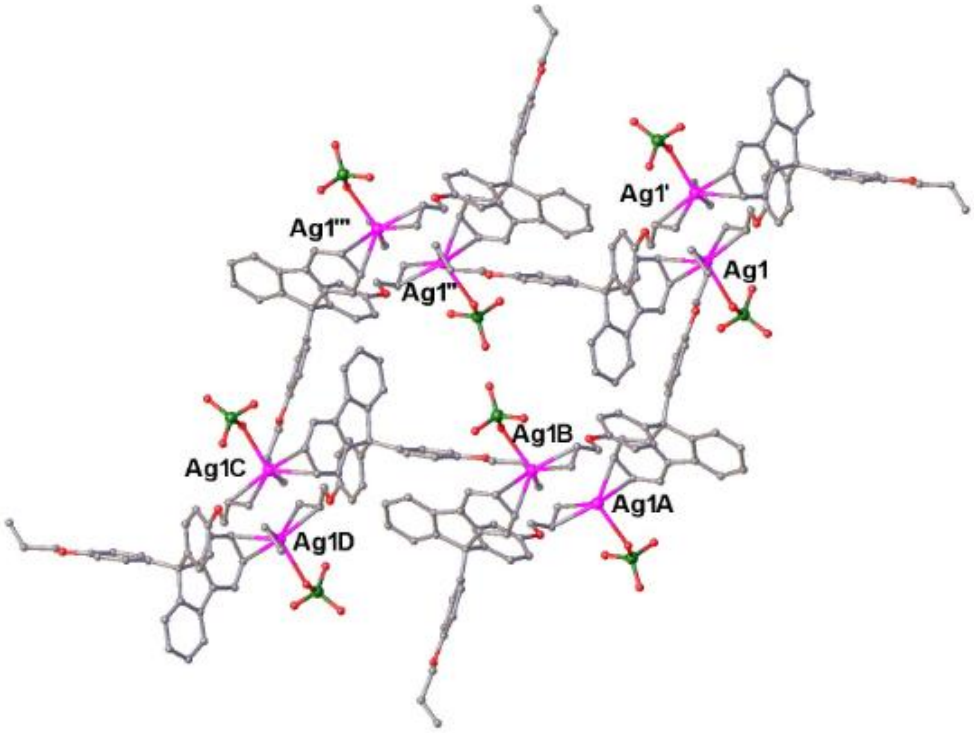


Figure 2.22 *– The asymmetric unit of complex* ***2.35****. The disordered allyloxy arm, the perchlorate anion and silver coordinated with water molecule are shown in dashed bonds.*

The overall structure of the complex is a 2D polymeric assembly, which involves the interaction of the ligand with three silver atoms through the fluorene aromatic ring and the olefins of the allyloxy arms. The ligand interacts with silver in a tridentate manner through the olefin group and also through the aromatic ring of the fluorene in a η^2-type interaction. Each silver atom coordinates with one oxygen atom of the perchlorate anion, two olefin groups and an aromatic ring in η^2-type coordination, as shown in Figure 2.23A. The 2D polymeric assembly is composed of a large four membered ring, in which each corner of the ring is also composed of smaller four membered rings, as shown in Figure 2.23B.



A)



B)

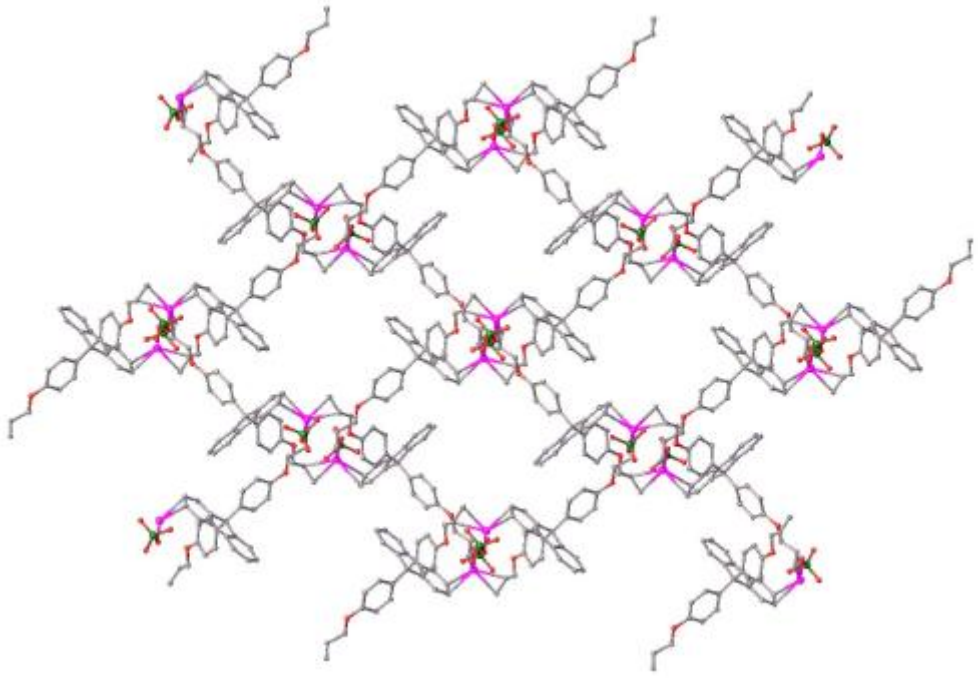
Figure 2.23 *- A) The smaller four membered ring at each corner of the big four membered ring. B) The bigger four membered ring that constitutes the 2D polymeric assembly. Selected bond lengths (Å) and angles (°): Ag1-C9 2.598(4), Ag1-C10 2.568(4), Ag1-C9,C10 2.486(4), Ag1-O4 2.485(3), Ag1-C21 2.469(4), Ag1-C22 2.432(4), Ag1-C21,C22 2.350(4), Ag1-C30 2.596(4), Ag1-C31 2.521(4), Ag1-C30,C31 2.470(4), O4-Ag1-C9,C10 98.5(2), O4-Ag1-C21,C22 100.9(1), O4-Ag1-C30,C31 104.5(1), C9,C10-Ag1-C21,C22 109.8(2), C9,C10-Ag1-C30,C31 119.3(1), C21,C22-Ag1-C30,C31 119.4(2).*

Silver is four coordinate with the largest and the second largest bond angles measured between the centroids of the olefin and the η^2-type linked aromatic ring. The values of the two largest bond angles are almost the same with bond angles of 119.4° and 119.3°. The calculated τ_4 value is 0.86, revealing a trigonal pyramidal geometry. All the individual silver-carbon bonds as well as

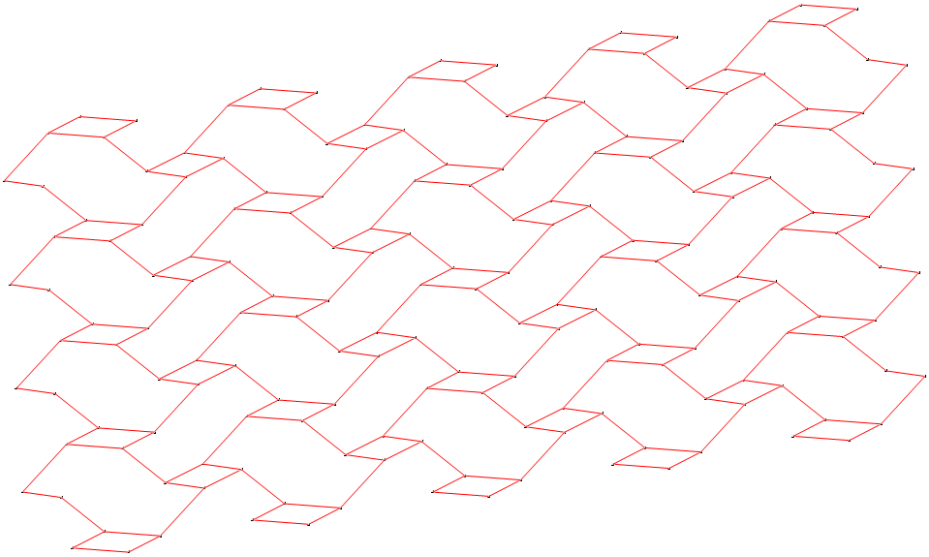
the distance from the centroid of the olefin group or the aromatic ring are longer than the silver-carbon bonds measured elsewhere in this project.

The four membered ring shown in Figure 2.23A, is composed of two ligands through the coordination of the olefin group of one of the allyloxy arms and the fluorene aromatic ring with an Ag····Ag separation distance of 8.411 Å. The other allyloxy arm bridge adjacent four membered rings to form the bigger four membered ring with an Ag····Ag separation distance of 17.100 Å. In other words, the ligand bridges two adjacent silver atoms through the allyloxy arms with a separation distance of 17.100 Å. The four membered rings grow into a 2D polymeric assembly, as shown in Figure 2.24A.

Each silver atom is connected to three different ligands and each ligand is also connected to three different ligands; therefore, both the ligand and the silver atom are taken as nodes of the network. The network system can be expressed as 4.8^2 topology, as shown in Figure 2.24B, similar to the topology of complex **2.33**.



A)



B)

Figure 2.24 *– A) Part of the 2D polymeric assembly of complex* ***2.35*** *showing the four membered ring cavities. All the disorder and hydrogen atoms have been omitted for clarity. B) The network topology of complex* ***2.35****.*

*2.3.5 Complex of the diallylether of bisphenol A (**2.27**)*

With silver(I) tetrafluoroborate (**2.36**)

A solution of ligand **2.27** in acetone was mixed with two equivalents of silver(I) tetrafluoroborate solution in acetone. Diethyl ether diffusion into the reaction mixture for a week followed by slow evaporation of the solvent resulted in the growth of crystals suitable for X-ray structure analysis. The structure solved in the orthorhombic Pbca space group. The asymmetric unit contains one full ligand molecule, one silver atom and a non-coordinated tetrafluoroborate anion, revealing a 1:1 (metal:ligand) ratio complex, as shown in Figure 2.25.

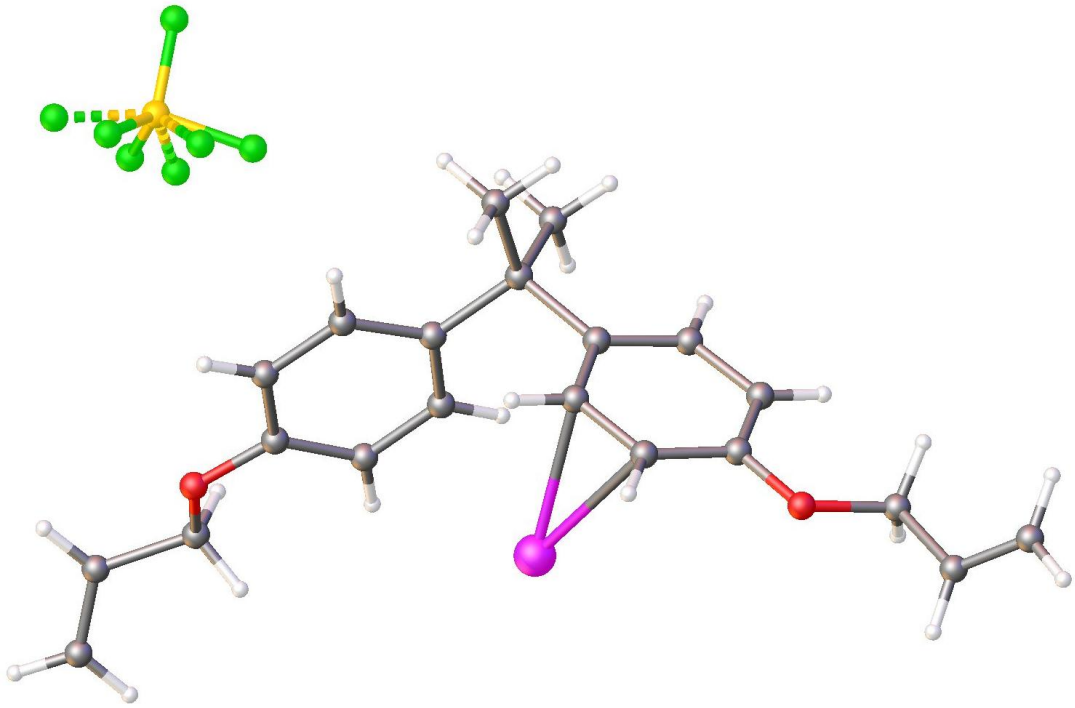


Figure 2.25 *– The asymmetric unit of complex* ***2.36****, showing the full ligand molecule, a silver atom and the disordered tetrafluoroborate anion. The minor site occupancy of the anion is shown in dotted bonds.*

As shown in Figure 2.25, the tetrafluoroborate anion has a rotational disorder with 51% dominant position occupancy.

The overall structure of the complex is a 2D polymeric assembly through the interaction of the olefin groups of the allyloxy arms and the aromatic ring in a η^2-type interaction with silver. The ligand acts as a tridentate bridging ligand by connecting three different symmetry related silver atoms.

As shown in Figure 2.26, the interaction of one of the allyloxy arms and the aromatic ring with silver forms a four membered ring with an Ag1····Ag1' separation distance of 7.897 Å, which acts as the longer side of the four membered ring. In this ring, the silver atom acts as a bridging metal atom, which constitutes the shorter side of the four membered ring with a separation distance of 4.096 Å, measured between the centroids of the coordinated olefin and arene groups. The other half of the ligands bridge two adjacent four membered rings through the other allyloxy arms.

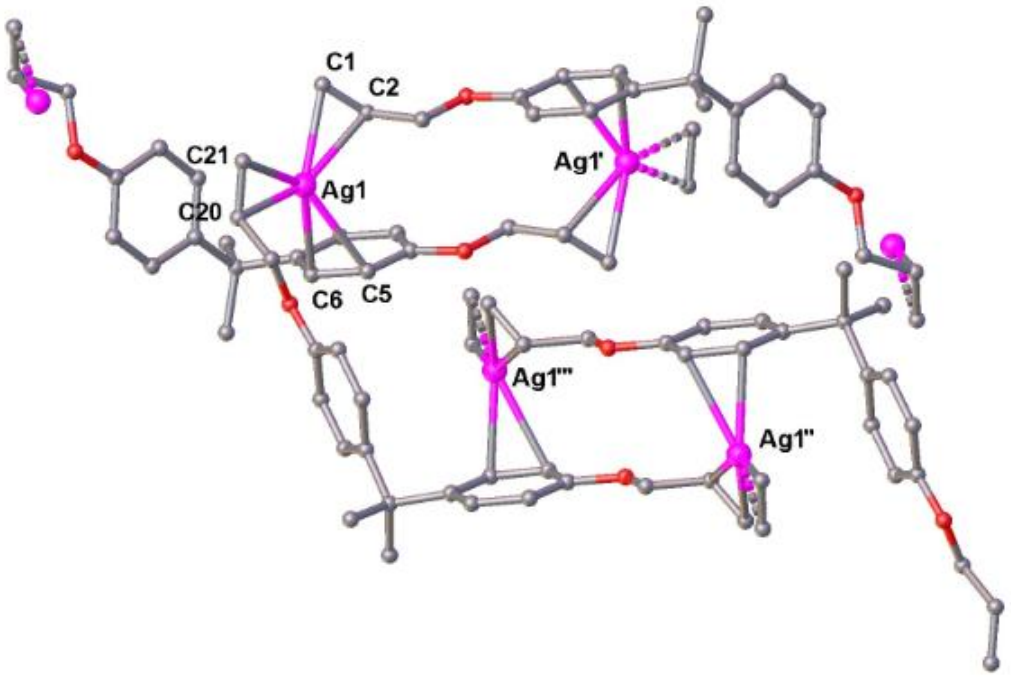


Figure 2.26 *– Part of the 2D polymeric assembly of complex* ***2.36****. All hydrogen atoms and the tetrafluoroborate anions have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-C5 2.653(2), Ag1-C6 2.493(2), Ag1-C5,C6 2.479(2), Ag1-C1 2.425(1), Ag1-C2 2.422(1), Ag1-C1,C2 2.333(1), Ag1-C20 2.408(2), Ag1-C21 2.398(2), Ag1-C20,C21 2.309(2), C5-Ag1-C1 124.9(2), C5-Ag1-C2 93.6(2), C6-Ag1-C1 134.5(2), C6-Ag1-C2 110.0(2), C5,C6-Ag1-C1,C2 116.7(2), C5-Ag1-C21 139.8(2),C5-Ag1-C20 110.5(2), C6-Ag1-C21 130.6(2), C6-Ag1-C20 99.1(2), C5,C6-Ag1-C20,C21 121.4(2), C2-Ag1-C21 119.3(2), C2-Ag1-C20 150.8(2), C1-Ag1-C21 91.4(2), C1-Ag1-C20 123.3(2), C1,C2-Ag1-C20,C21 121.5(2).*

Interestingly, all the silver-ligand interactions in this complex are through the C=C double bonds of the olefin and arene with a η^2-type interaction.

The silver atoms are three coordinate with almost similar angles (121.4°, 121.5° and 116.7°) between the centroids of the interacted olefin and arene C=C groups. From the measured bond angles the silver atom has a trigonal planar geometry. The silver-carbon bond distance measured for the arene

carbons (Ag1-C5,C6) is longer than the measured bond distances for the corresponding silver-carbon bond distances with the olefin groups. Even though the individual silver-carbon bond distances measured for the silver-arene interaction (Ag1-C5, 2.653 Å and Ag1-C6 2.493 Å) are relatively long, the distance measured between silver and the centroid of the arene group (Ag1-C5,C6 2.479 Å) is in the expected range for such interactions.

Since each silver atom is connected to three different ligands and also each ligand is connected to three different silver atoms, both the silver atom and the ligand are taken as nodes of the 2D network. Like complexes **2.35** and **2.33** the 2D network topology is 4.8^2, as shown in Figure 2.27.

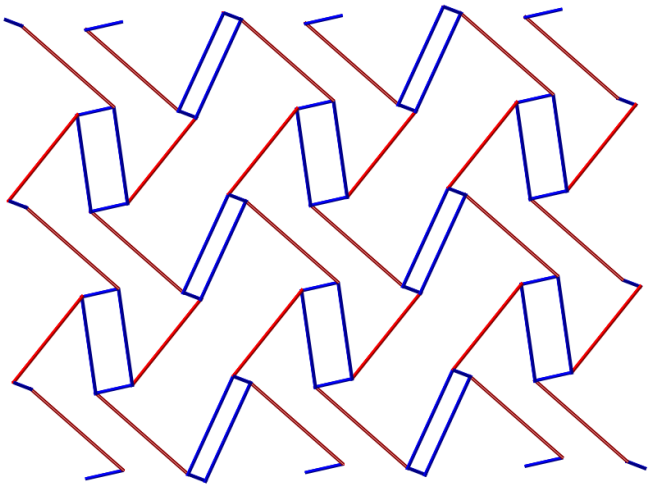


Figure 2.27 *– The 2D 4.8^2 topology network of complex* ***2.36****.*

In our earlier work using ligand **2.27** and silver perchlorate, a double helical structure was found that incorporates the perchlorate anion and the olefin groups of the two allyloxy arms,[124] as shown in Figure 2.28.

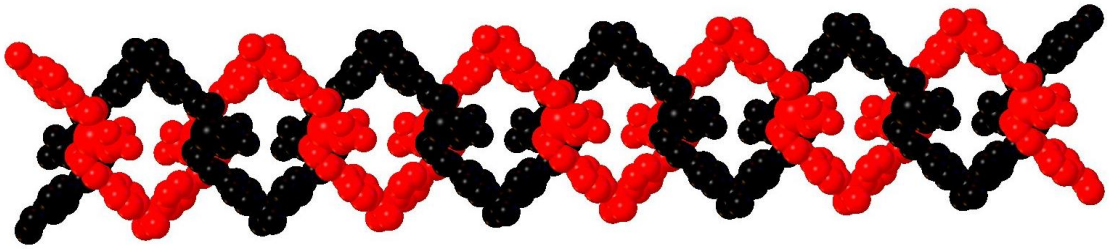


Figure 2.28 *– Space filling diagram of the double helix structure of ligand* ***2.27*** *with silver(I) perchlorate.*[124]

It seems the absence of a coordinating anion played a significant role in the 2D polymeric assembly of complex **2.36**, which involves the interaction of the arene group in addition to the olefins. Therefore, the importance of the anion on the assembly of the structure of the complex is shown in these two assemblies.

*2.3.6 Complexes of cyclohexylidenedi(4-allyloxyphenyl)methane (**2.31**)*

With silver(I) perchlorate (**2.37**)

Ligand **2.31** was reacted with silver(I) perchlorate, which resulted in the growth of crystals of complex **2.37** by using diethyl ether diffusion into the reaction mixture. The structure was solved in the monoclinic $P2_1/c$ space group.

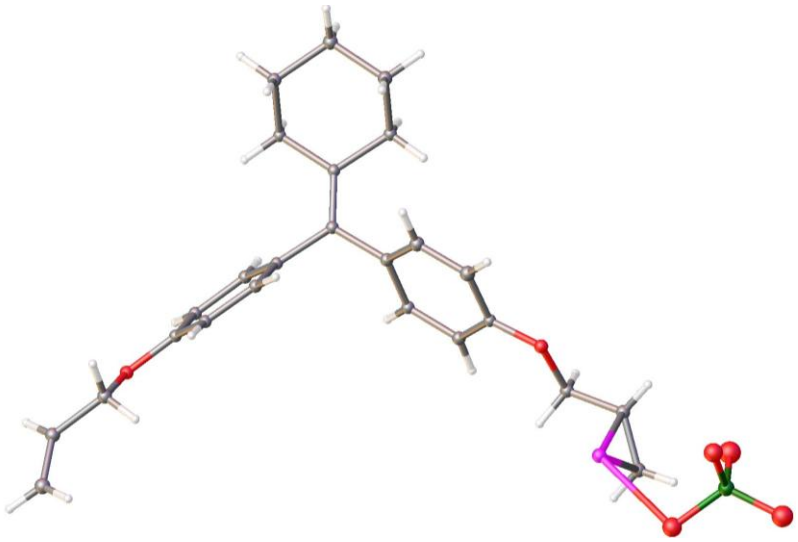


***Figure 2.29** – The asymmetric unit of complex **2.37**.*

The asymmetric unit, shown in Figure 2.29, contains one full ligand molecule, one silver atom and a perchlorate counter anion, revealing a 1:1(metal:ligand) ratio or an M_1L_1 type coordination complex.

The structure grows into a 1D polymeric assembly through the interaction of the olefin groups of the ligand. The ligand bridges symmetry related adjacent silver atoms through the allyloxy arms. In addition to the olefin groups from the neighbouring ligands, the silver atom is also connected with the perchlorate counter anion, which makes the silver atom three coordinate. The largest

bond angle around the environment of the silver atom is measured between the centroids of the connected olefin groups, while the second and third are measured between the perchlorate oxygen and the centroids of the olefins. The (C1,C2-Ag1-C18,C19 138.9°) is the largest bond angle, (O6-Ag1-C18,C19 108.3°) and (O6-Ag1-C1,C2 102.6°) are the second and third bond angles around the environment of the tri coordinated silver atom, as shown in Figure 2.30.

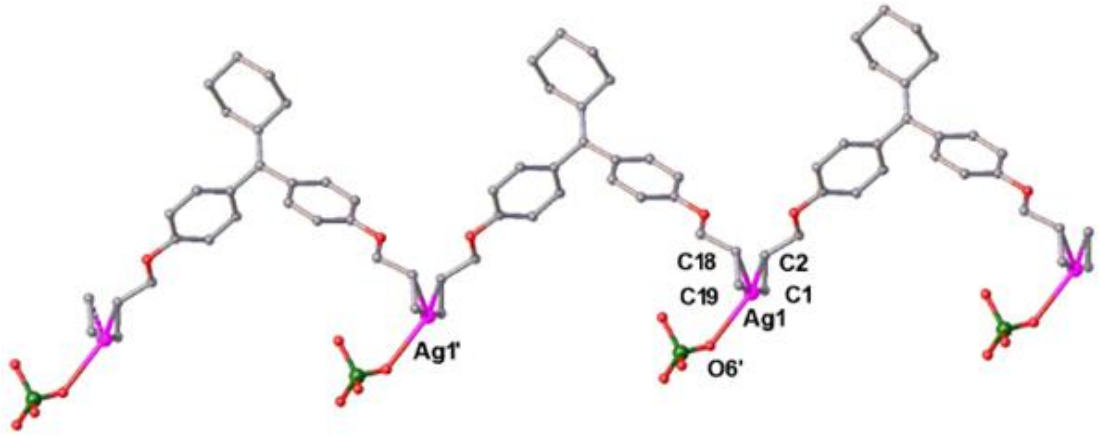


Figure 2.30 *– Part of the 1D polymeric assembly of complex* ***2.37****. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C1 2.357(1), Ag1-C2 2.404(1), Ag1-C1,C2 2.285(1), Ag1-C18 2.430(2), Ag1-C19 2.360(4), Ag1-C18,C19 2.298(3), Ag1-O6 2.576(1), O6-Ag1-C1 91.6(3), O6-Ag1-C2 112.7(3), O6-Ag1-C1,C2 102.6(3), C18-Ag1-O6 120.7(2), C19-Ag1-O6 95.0(2), C18,C19-Ag1-O6 108.3(2), C18-Ag1-C1 139.0(2), C18-Ag1-C2 106.9(2), C19-Ag1-C1 171.5(2), C19-Ag1-C2 139.2(2), C18,C19-Ag1-C1,C2 138.9(2).*

From the measured bond angles around the environment of the silver atom, there is a big distortion from the ideal 120° angle for trigonal planar geometry.

All the silver-carbon bond lengths measured are in the expected range for such interactions; however, the silver-oxygen bond length measured between Ag1 and O6 (2.576 Å) is relatively long but it is still within the expected bond length range for silver-oxygen interactions.[110] The ligand acts in a bidentate

manner that bridges adjacent silver atoms with an Ag1···Ag1' separation distance of 12.427 Å, which is shorter than the separation distance measured between adjacent silver atoms in the complex of ligand **2.27** with silver(I) perchlorate (13.783 Å).[124]

Interestingly, no interaction of the aromatic ring or the alkene functional group at the junction of the cyclohexane and the bisphenol moiety with silver is observed. Ligand **2.31** is quite similar to ligand **2.27** but the structure of complex **2.36** involves the coordination of the aromatic ring at the expense of the non-coordinating counter anion.

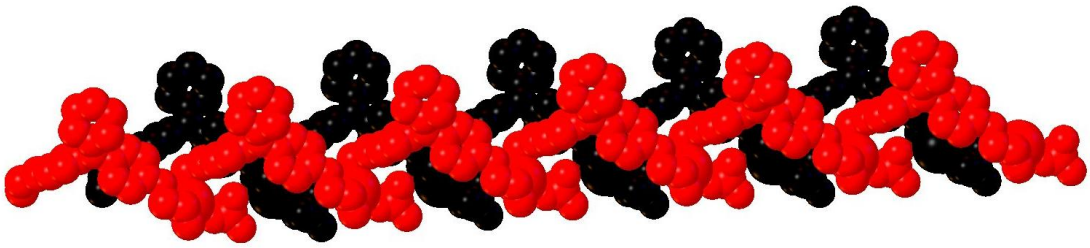


Figure 2.31 *– Two strands of the side-by-side 1D polymeric assembly of complex* ***2.37****. Both strands are growing in the same direction.*

With silver(I) triflate (**2.38**)

Using the same crystal growth method as for complex **2.37**, ligand **2.31** was reacted with silver(I) triflate. The crystal structure was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains one full ligand molecule, one silver atom, a coordinated water molecule and a non-coordinating triflate counter anion in a 1:1 (metal:ligand) ratio or an M_1L_1 type coordination complex, as shown in Figure 2.32.

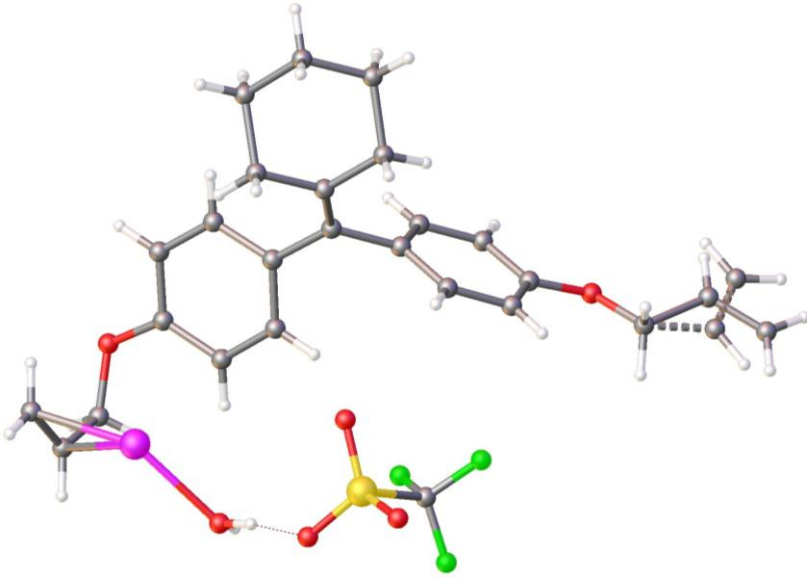


Figure 2.32 *– The asymmetric unit of complex* ***2.38****. The disorder in the allyloxy arm is shown with broken bonds.*

As shown in Figure 2.32, one of the allyloxy arms of the ligand has a disorder over two sites with 50% position occupancy for both sites. In this project, disorder with 50% site occupancy is a rare event. Similar to complex **2.37**, the overall structure of complex **2.38** is a 1D polymeric structure.

Silver is three coordinate through the interaction of two olefins and a water molecule, as shown in Figure 2.33. The largest bond angle around the environment of silver is (132.8°) and is measured between the centroid of the olefins (C1,C2-Ag1-C24,C25). The other two angles (120.9° and 106.3°) are measured between the oxygen atom of the water molecule (O4) and the centroid of the two olefins. From the measured bond angles the silver atom has a distorted tigonal geometry. Similar to complex **2.37**, the ligand is acting in a bridging bidentate mode by connecting two adjacent silver atoms with an Ag1···Ag1' separation distance of 12.081 Å, which is shorter than the separation distance measured in complex **2.37**.

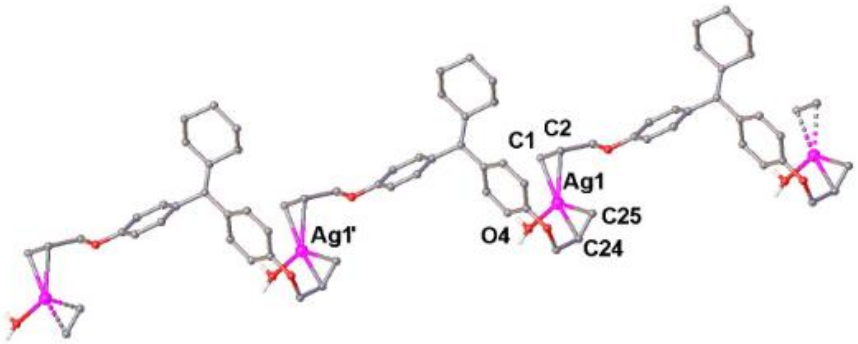


Figure 2.33 *– Part of the 1D polymeric assembly of complex* ***2.38****. All hydrogen atoms and the triflate counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C1 2.418(4), Ag1-C2 2.419(4), Ag1-C1,C2 2.329(4), Ag1-C24 2.435(2), Ag1-C25 2.345(2), Ag1-C24,C25 2.294(2), Ag1-O4 2.270(1), C24-Ag1-O4 105.3(2), C25-Ag1-O4 136.9(2), C24,C25-Ag1-O4 120.9(2), C24-Ag1-C1 162.6(1), C24-Ag1-C2 132.7(1), C25-Ag1-C1 132.4(1), C25-Ag1-C2 101.1(1), C24,C25-Ag1-C1,C2 132.8(1), O4-Ag1-C1 90.7(1), O4-Ag1-C2 121.8(1), O4-Ag1-C1,C2 106.3(1).*

Having a coordinated water molecule with a triflate counter anion in the complex is a good recipe for hydrogen bonding between the oxygen atoms of the triflate and the water molecules. There is indeed hydrogen bonding between the water molecule and the triflate counter anion that transforms the 1D structure into a 2D polymeric assembly, as shown in Figure 2.34. Each triflate counter anion has two hydrogen bonding interactions and each water molecule also has two hydrogen bonding interactions, with the measured angles and distances shown in table 2.2.

D-H⋯A	D-H	H⋯A	D⋯A	D-H⋯A
O-H⋯O	0.808	1.966	2.765	170.566
O-H⋯O	0.816	1.973	2.769	164.772

Table 2.2 *Hydrogen bonding geometry between the water molecule and the triflate counter anion.*

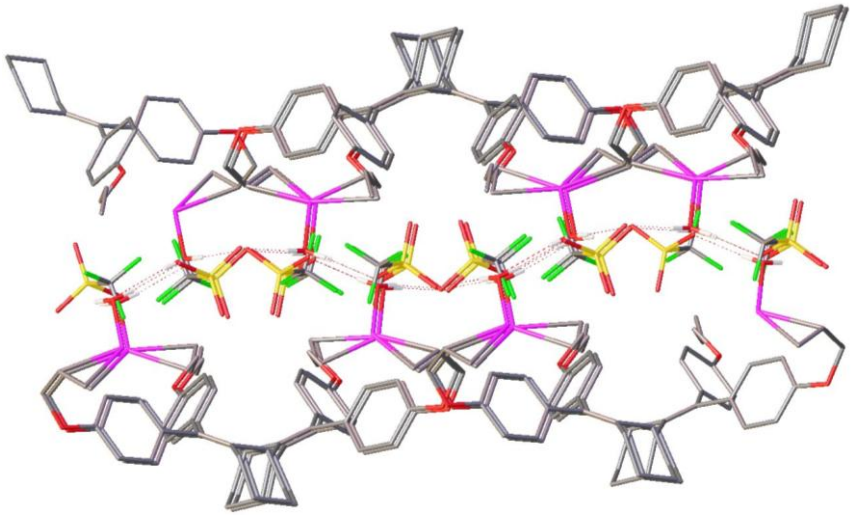


Figure 2.34 *– The 2D polymeric assembly of complex* ***2.38*** *due to hydrogen bonding between the water molecule and the triflate counter anion. All hydrogen atoms except for the water molecule have been excluded.*

Considering the other site occupancy of the disordered allyloxy arm does not make any difference on the overall structure of the complex. The structures of both **2.37** and **2.38** are quite similar, except for the presence of hydrogen bonding in complex **2.38**, which turns the 1D assembly into 2D assembly.

Generally, the structures of ligands **2.20**, **2.21**, **2.26**, **2.27**, and **2.31** are similar to each other except for the group at the junction of the two aryl rings of the bisphenol moiety, but various 1D and 2D polymeric assemblies were obtained depending on the type of the group introduced at the junction and also the counter anion used.

2.3.7 Complex of the diallylether of bisphenol P (2.32)

With silver(I) tetrafluoroborate (**2.39**)

Crystals of a complex of the diallylether of bisphenol P (**2.32**) with silver(I) tetrafluoroborate were grown using diethyl ether diffuision into the reaction mixture. The structure of the complex solved in the monoclinic $P2_1/m$ space group. The asymmetric unit contains half a ligand molecule, half a coordinated water molecule, half a silver and half a non-coordinated tetrafluoroborate counter anion revealing a 1:1 (ligand:metal) ratio or M_1L_1 type coordination complex, as shown in Figure 2.35. The silver atom is disordered over two positions and shown in faded pink colour. The corresponding bonding with the C=C and the water molecule is shown in broken lines.

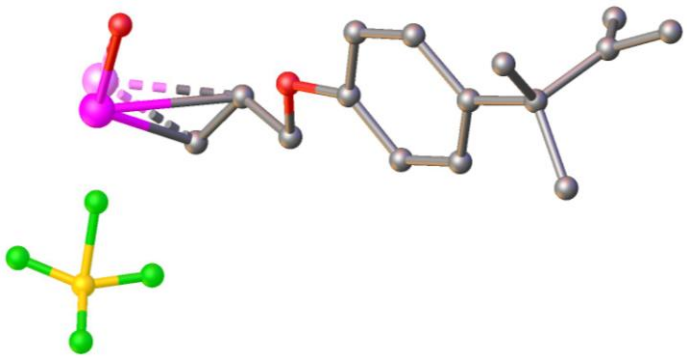


Figure 2.35 *– The asymmetric unit of complex* ***2.39****, showing half of the ligand molecule coordinated with a disordered silver atom over two sites. The minor site is shown in light pink colour with broken lines. All hydrogen atoms are removed for clarity.*

The overall structure is a 1D zigzag polymeric assembly, in which the ligand bridges adjacent silver atoms through the olefin groups, as shown in Figure 2.36. Even though we tried to collect the data of this complex using three different crystals that were grown from different solvents, the disorder of the structure makes the refinement very poor. The best refinement value for this complex is R_1 = 10.38% and was obtained using acetone as solvent for both the ligand and silver(I) tetrafluoroborate.

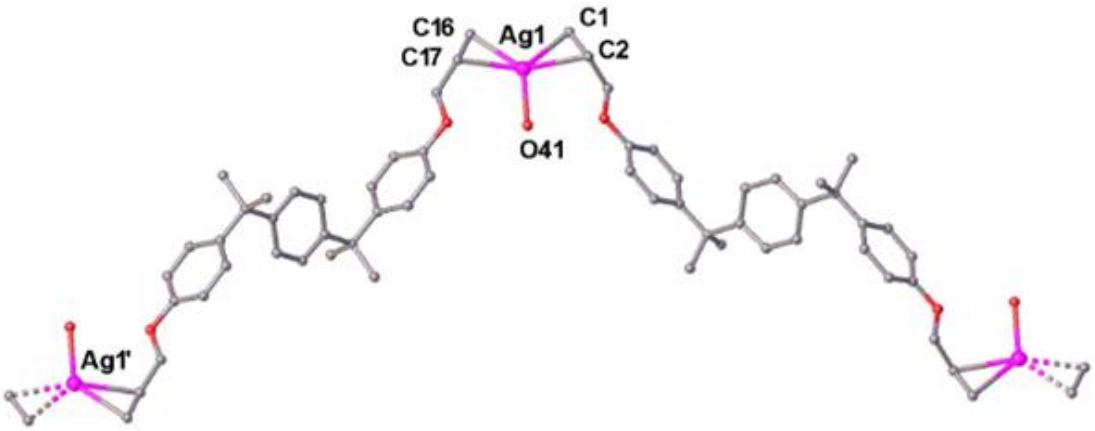


Figure 2.36 *– Part of the 1D zigzag polymeric structure of complex* ***2.39****. All hydrogen atoms, the disordered silver atom and the tetrafluoroborate anion have been omitted for clarity.*

An interesting feature of this structure is the separation distance measured between Ag1 and Ag1'. This is 21.485 Å, which results from the introduction of a spacer aromatic ring at the junction of the bisphenol moiety. This spacer aromatic ring introduction significantly increases the separation distance between adjacent silver atoms compared to the previous complexes formed from ligands with two allyloxy arms. In fact the separation distance measured between the two silver atoms are similar to the complex formed from ligand **2.32** with silver perchlorate, which was reported in my BSc. Honours project.[124]

2.4 Ligands containing three allyloxy groups

After studying the interactions of ligands containing one and two allyloxy groups with different silver(I) salts the next step was to investigate ligands containing three allyloxy groups. For this, the following three ligands were used.

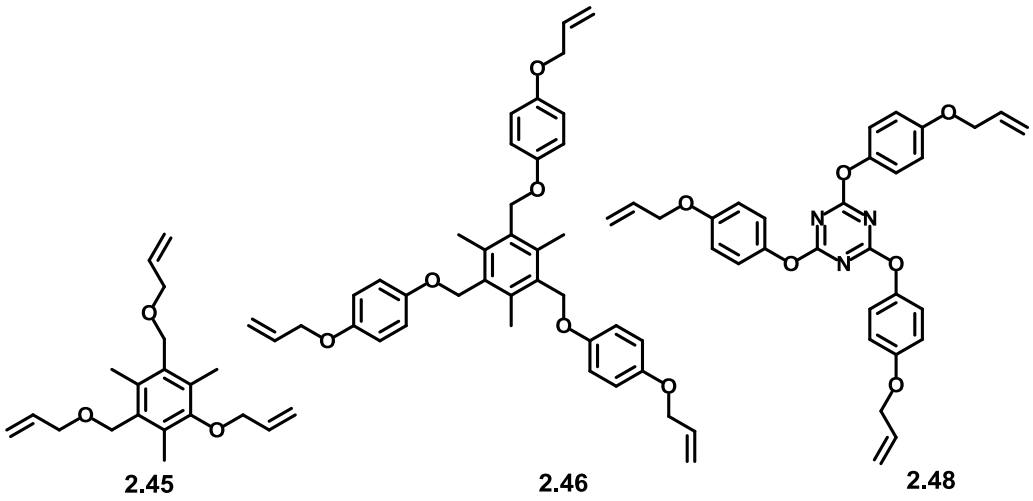
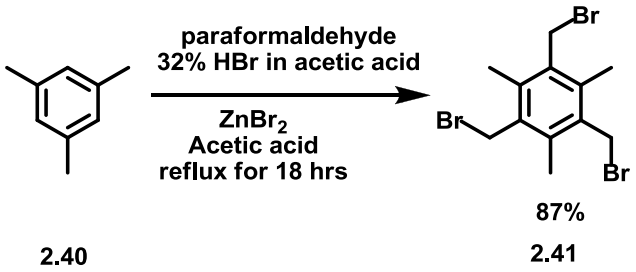


Figure 2.37 *– Compounds used to investigate the coordination chemistry of ligands containing three allyloxy groups.*

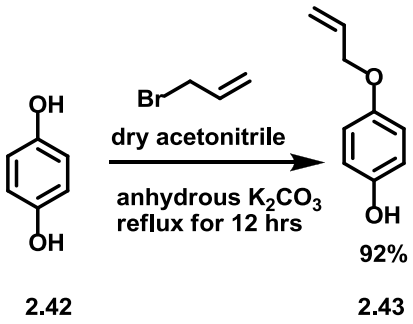
2.4.1 Syntheses of ligands containing three allyloxy groups and their precursors.

One of the precursors for the syntheses of ligands **2.45** and **2.46** is 1,3,5-tri(bromomethyl)-2,4,6-trimethylbenzene (**2.41**), which was synthesised from the commercially available 1,3,5-trimethylbenzene (mesitylene) (**2.40**) using a literature method,[149] as shown in scheme 2.4.



Scheme 2.4 *- The synthesis of precursor **2.41**.*

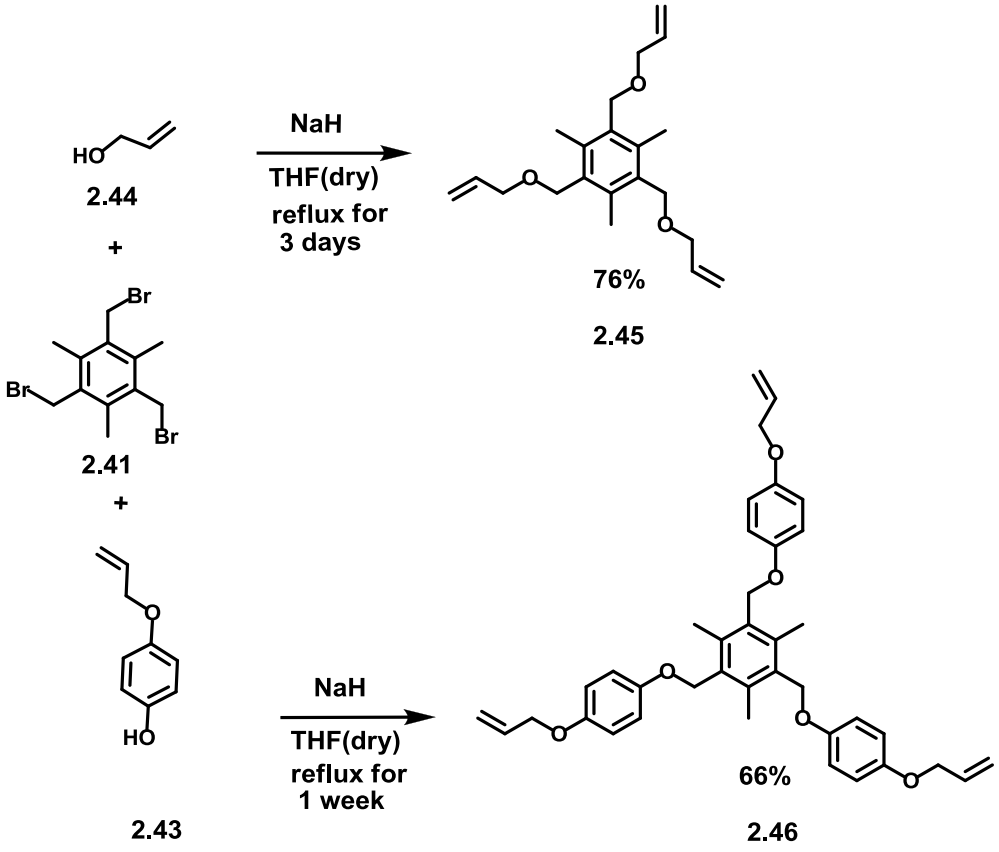
One of the precursors for the syntheses of ligands **2.46** and **2.48** is 4-allyloxyphenol (**2.43**), which was synthesised from the commercially available 1,4-dihydroxybenzene (hydroquinone) (**2.42**) using a literature method,[150] as shown in scheme 2.5.



Scheme 2.5 – *The synthesis of precursor* ***2.43****.*

Ligands **2.45** and **2.46** were synthesised from precursor **2.41** by reacting with allyl alcohol (**2.44**) and 4-allyloxyphenol (**2.43**) respectively, using a common method[151] shown in scheme 2.6. Ligand **2.45** is an oily liquid and was characterised by ^{1}H NMR, ^{13}C NMR, mass spectrometry and infrared spectroscopy.

Ligand **2.46** is a white powder and crystals were grown from ethanol. In addition to the mentioned characterisation methods for ligand **2.45**, ligand **2.46** was characterised by melting point, elemental analysis and X-ray crystal structure. The structure of ligand **2.46** solved in the triclinic P-1 space group and the asymmetric unit contains one full ligand molecule, as shown in Figure 2.38.



Scheme 2.6 *– The syntheses of ligands* ***2.45*** *and* ***2.46*** *from precursor* ***2.41*** *and their respective hydroxyl containing precursors (****2.44*** *and* ***2.43****).*

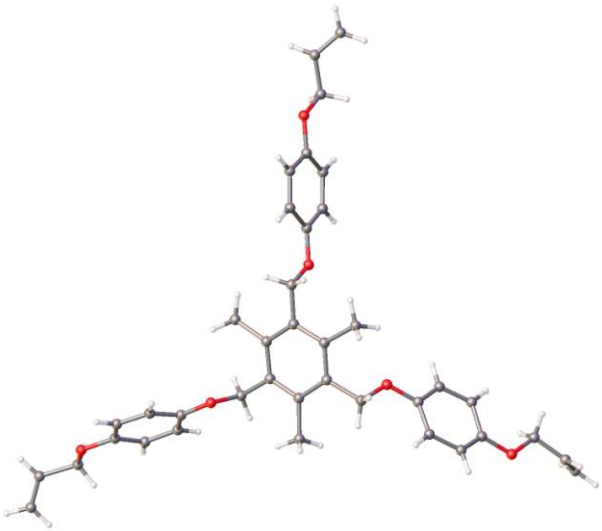
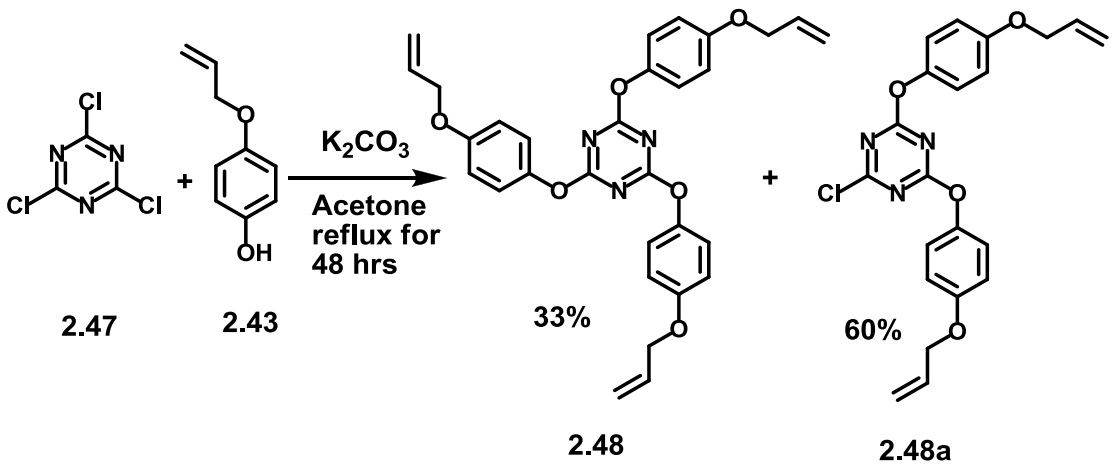


Figure 2.38 *– The X-ray structure of ligand* ***2.46***

Ligand **2.48** was synthesised from precursor **2.43** and the commercially available cyanuric chloride (**2.47**), as shown in scheme 2.7.[152]



Scheme 2.7 *– The synthesis of ligand* ***2.48*** *from precursors* ***2.43*** *and* ***2.47****.*

Ligand **2.48** is a white crystalline compound and was characterised by similar methods as in the case of ligand **2.46**, except for the X-ray structure analysis.

2.4.2 Complex of 1,3,5-tris(allyloxymethyl)-2,4,6-trimethylbenzene (2.45)

With silver(I) triflate (**2.49**)

A solution of ligand **2.45** was mixed with three equivalents of silver triflate in acetone. Diethyl ether diffusion into the reaction mixture resulted in the growth of crystals suitable for X-ray crystal structure analysis. The structure was solved in the monoclinic C2/c space group. The asymmetric unit contains one full ligand molecule, one and half silver atoms, one coordinated triflate counter anion and a disordered non-coordinated triflate anion, revealing a 2:3 (ligand:metal) ratio or an M_3L_2 type coordination complex, as shown in Figure 2.39. One of the silver atoms and the non-coordinated triflate anion have half occupancies, while the other silver atom and triflate anion have full occupancy. The silver atom with half occupancy lies on a twofold rotation axis. The non-coordinated triflate anion is also on a twofold rotation axis in which the same site is occupied by the $–CF_3$ and SO_3 groups.

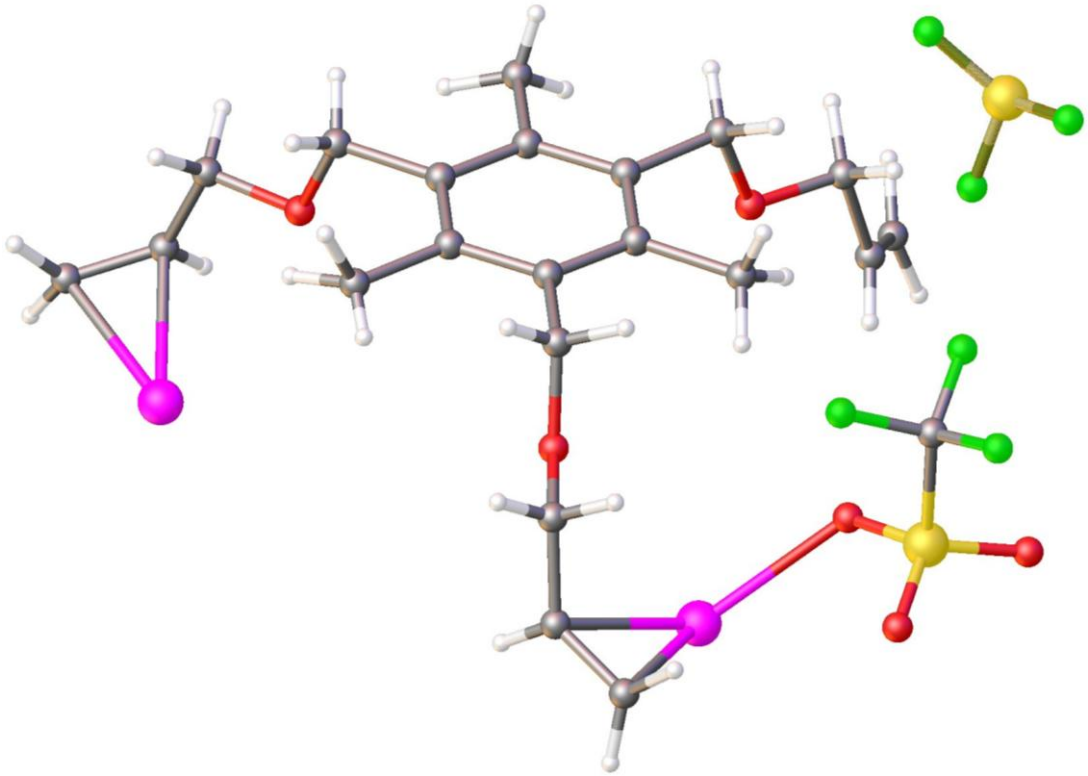


Figure 2.39 *– The asymmetric unit of complex* ***2.49****, showing the full ligand molecule, two silver atoms (one of them has half occupancy) and also the triflate anions. The non-coordinated triflate anion lies on a twofold rotation axis.*

The overall structure of the complex is a 2D polymeric structure, which involves the interaction of the three allyloxy arms with silver atoms. One of the silver atoms (Ag2) interacts with two allyloxy arms of **2.45** (C16=C17 and C12A=C13A), while the other silver atom (Ag1) interacts with the third allyloxy arm (C20=C21, C20A=C21A), as shown in Figure 2.40. Ag2 interacts with the oxygen atoms (O5A and O6A) of two triflate anions, while Ag1 interacts with one oxygen atom (O7 and O7A) from the third triflate counter anion. Ag2 bridges two symmetrically independent allyloxy arms of the ligand as well as oxygen atoms of the triflate counter anion, while Ag1 bridges a symetrically related allyloxy arm of the ligand as well as oxygen atom of the triflate counter anion. All the silver-carbon interactions between the centroid of the olefin group as well as the individual silver-carbon bond lengths are in the expected bond length range for such types of interactions. The silver-oxygen

interactions between silver and the oxygen atoms of the triflate anions are also in the expected range for silver-oxygen interactions.[110]

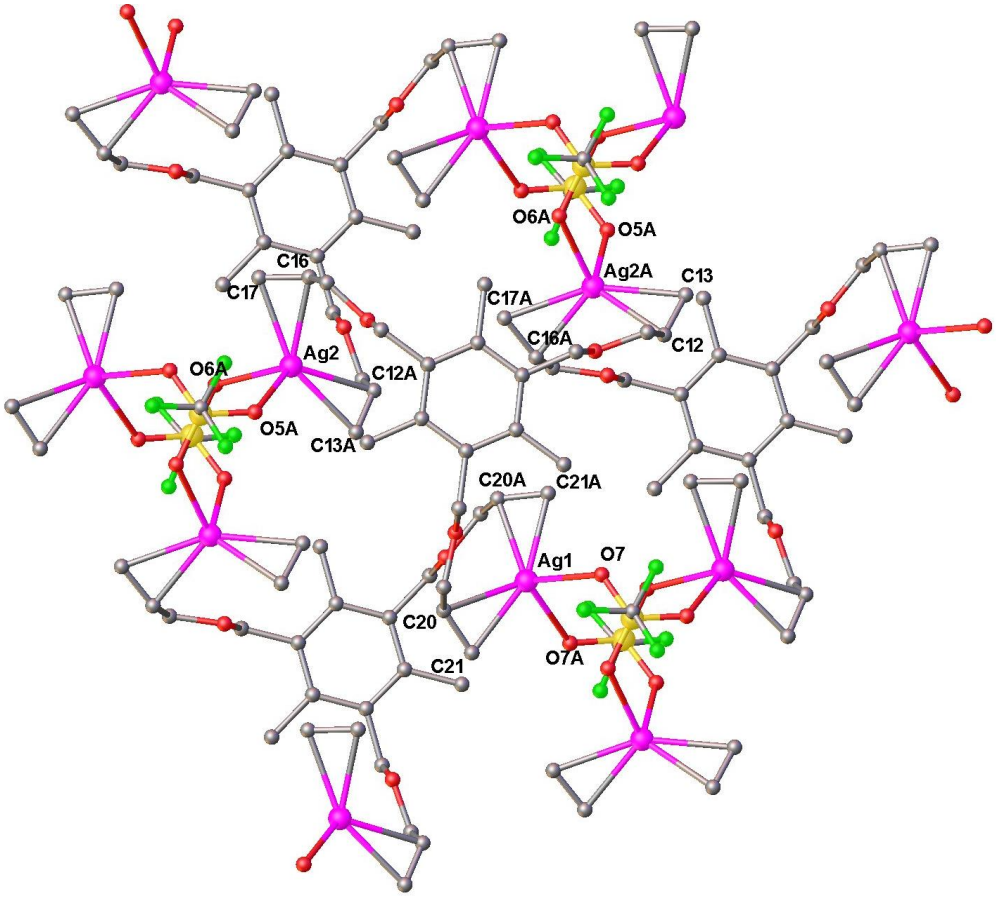


Figure 2.40 *– Part of the 2D polymeric assembly of complex* ***2.49****. All hydrogen atoms and the non-coordinated triflate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C20 2.434(2), Ag1-C21 2.399(2), Ag1-C20,C21 2.322(2), Ag1-O7 2.440(3), Ag1-C20A 2.434(2), Ag1-C21A 2.399(2), Ag1-C20A,C21A 2.322(2), Ag1-O7A 2.440(2), O7-Ag1-O7A 92.7(2), O7-Ag1-C20,C21 115.3(2), O7-Ag1-C20A,C21A 100.4(2), O7A-Ag1-C20,C21 100.4(2),O7A-Ag1-C20A,C21A 115.3(2), C20,C21-Ag1-C20A,C21A 127.8(2), Ag2-C16 2.401(2), Ag2-C17 2.418(2), Ag2-C16,C17 2.315(2), Ag2-O5 2.429(4), Ag2-O6 2.431(3), Ag2-C12 2.428(2), Ag2-C13 2.407(2), Ag2-C12,C13 2.324(2), O5-Ag2-O6 92.6(1), O5-Ag2-C16,C17 108.4(2), O5-Ag2-C12,C13 107.0(2), O6-Ag2-*

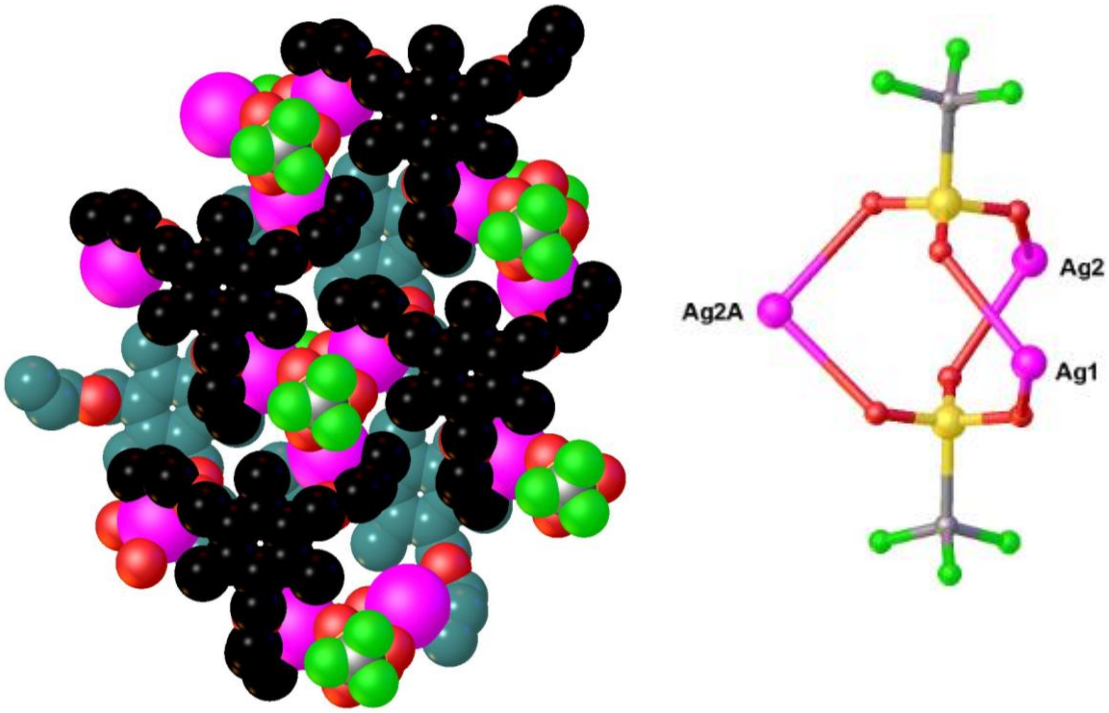
C16,C17 103.5(2), O6-Ag2-C12,C13 112.6(2), C16,C17-Ag2-C12,C13 127.3(2).

Ag1 is four coordinate from two symmetrically related olefin groups and also symmetrically related oxygen atoms of the triflate counter anions. The largest bond angle around the environment of Ag1 is 127.8° and is measured between the centroids of the olefin groups. The calculated τ_4 value for Ag1 is 0.83, revealing a trigonal pyramidal shape.

Ag2 is also four coordinate from two independent olefin groups and oxygen atoms of the triflate counter anions. The largest bond angle around the Ag2 environment is 127.3° and is measured between the centroids of the olefins. The second and third largest bond angles around Ag2 are between the oxygen atoms of the triflate anion and the centroids of the olefins (O6-Ag2-C12,C13 and O5-Ag2-C16,C17 respectively) with bond angles of 112.6° and 108.4°. The calculated τ_4 value for Ag2 is 0.85, revealing a trigonal pyramidal geometry. Interestingly, the calculated τ_4 values as well as the largest bond angles measured around both Ag1 and Ag2 are similar.

The ligand is acting in a tridentate bridging manner that links three silver atoms with Ag···Ag separation distances of 7.779 Å, 8.003 Å and 8.181 Å.

An interesting feature of this structure is the way the allyloxy arms are positioned in order to interact with silver. The allyloxy arms are all positioned on the same side of the plane of the central aromatic ring of the ligand. Moreover, the ligands are positioned in such a way that two aromatic rings do not have π-π interactions, as shown in Figure 2.41A. The allyloxy arms of the ligands from the top layer of the complex are positioned downwards, while the allyloxy arms from the bottom layer are positioned upwards and the silver atoms are sandwiched between the layers. The cavity between the ligands is occupied by the triflate anions. The triflate anions are interacting with three silver atoms through the three oxygen atoms of the anion. Similar to the silver-ligand interaction, the triflate anions also bind from the top and bottom of the plane of the silver atom, as shown in Figure 2.41B. Therefore, the silver atoms are also sandwiched between the triflate anions.



A) B)

Figure 2.41 *– A) The space filling structure of complex* ***2.49****, the black color show the coordination of the ligand from the top layer and the grey color from the bottom layer. The triflate anions fill the space formed between ligands. B) The triflate anions interaction from the top and bottom of the plane of the silver atoms of the complex.*

*2.4.3 Attempts to grow crystals of complexes of 1,3,5-tris(4-allyloxyphenoxymethyl)-2,4,6-trimethylbenzene (**2.46**)*

A number of attempts were made to grow crystals of complexes of ligand **2.46** with different silver(I) salts, using different solvents and methods of growing crystals, but no success was achieved.

*2.4.4 Complex of 2,4,6-tris(4-allyloxyphenoxy)-1,3,5-triazine (**2.48**)*

<u>With silver(I) perchlorate (**2.50**)</u>

A solution of ligand **2.48** was mixed with two equivalents of silver(I) perchlorate in acetone and diethyl ether diffusion into the reaction mixture

gave tiny crystals. The structure was solved in the monoclinic $P2_1/n$ space group with poor refinement (R_1=9.97%). The asymmetric unit contains one full ligand molecule, two silver atoms, two non-coordinated perchlorate anions, one coordinated and three non-coordinated acetone molecules, which reveals a 1:2 (ligand:metal) ratio or an M_2L_1 type coordination complex, as shown in Figure 2.42.

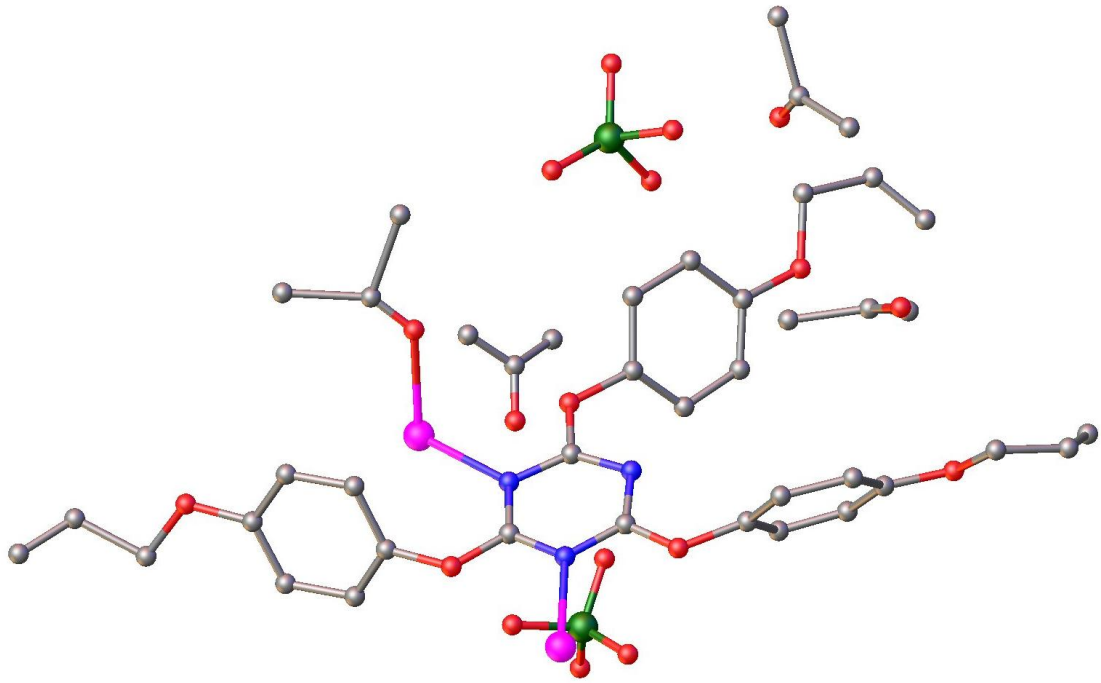


Figure 2.42 *– The asymmetric unit of complex* ***2.50****. All hydrogen atoms have been omitted for clarity.*

The overall structure of complex **2.50** is a 2D polymeric structure that involves the interaction of the three allyloxy arms and two of the nitrogen atoms of the triazine ring with silver, as shown in Figure 2.43. There are two symmetrically independent silver atoms, which are both three coordinate. One of them (Ag1) is bound by an olefin group, a nitrogen atom of a triazine ring and an acetone molecule, while the other (Ag2) has interactions with two olefins from adjacent ligands and a nitrogen atom of the triazine ring. It seems the interaction of each olefin group with silver is directed towards the nitrogen atom of the triazine ring of the adjacent ligand, so the central triazine ring has its own influence in the assembly of the structure, especially compared to ligand **2.46**.

In general, the ligand binds with silver atoms through five donor groups out of six possible sites, which makes **2.48** a pentadentate ligand.

As shown in Figure 2.43, each silver atom is doubly bridged by the allyloxy arms of the ligand in three directions, generating rectangles in each direction.

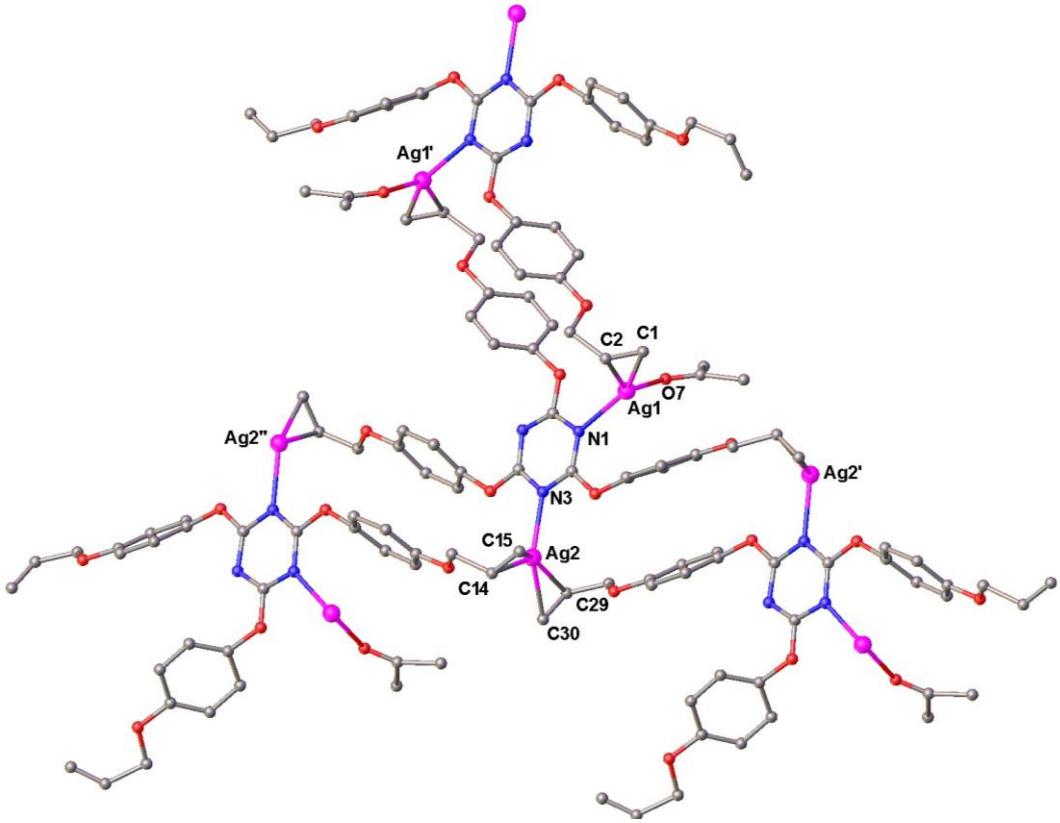


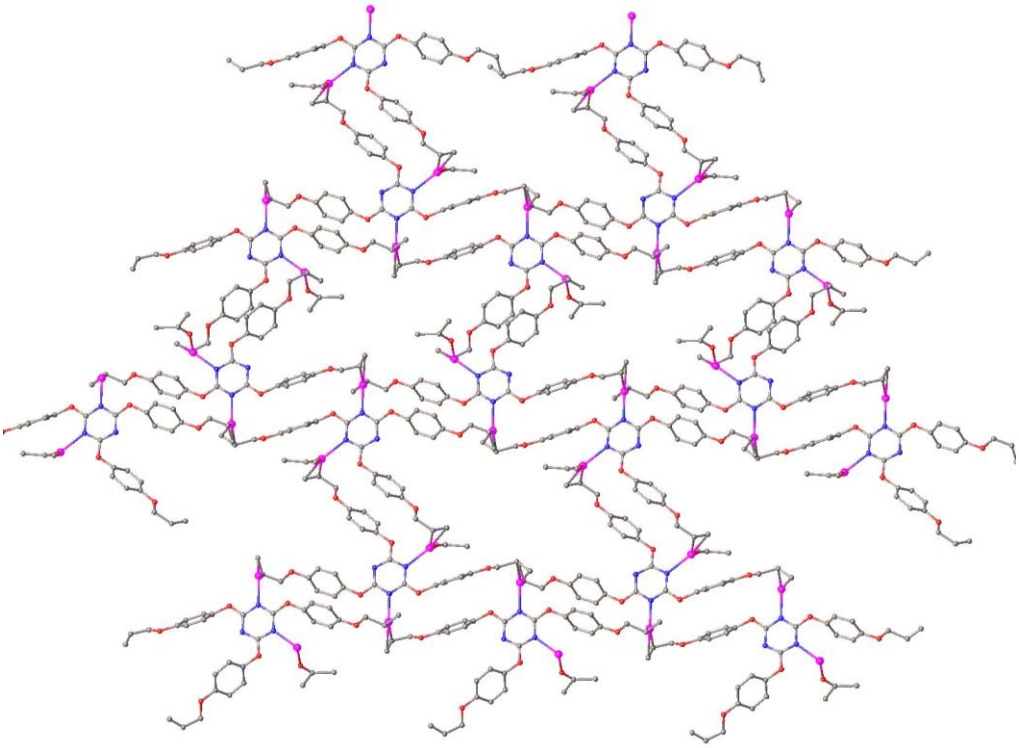
Figure 2.43 *– Part of the 2D polymeric assembly of complex* ***2.50****, showing the rectangular shapes formed in three directions due to the doubly bridging character of the ligand. All hydrogen atoms, non-coordinated acetone molecules and perchlorate anions are excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.292(2), Ag1-O7 2.302(2), Ag1-C1 2.283(1), Ag1-C2 2.323(1), Ag1-C1,C2 2.214(1), N1-Ag1-O7 98.4(4), N1-Ag1-C1,C2 130.2(4), O7-Ag1-C1,C2 127.8(2), Ag2-N3 2.239(2), Ag2-C14 2.454(1), Ag2-C15 2.547(1), Ag2-C14,C15 2.418(1), Ag2-C29 2.406(1), Ag2-C30 2.363(1), Ag2-C29,C30 2.289(1), N3-Ag2-C14,C15 106.2(4), N3-Ag2-C29,C30 122.2(4), C14,C15-Ag2-C29,C30 130.9(4).*

All the silver-carbon, silver-nitrogen and silver-oxygen bond lengths measured in this structure are in the expected ranges for each respective category.[110, 132, 153] The bond angles measured around the Ag1 environment are 130.2°, 127.8° and 98.4°, showing considerable distortion from the ideal trigonal planar geometry bond angle (120°). The bond angles (130.9°, 122.2° and 106.2°) measured around Ag2 also show distortions from the ideal trigonal planar shape (120°).

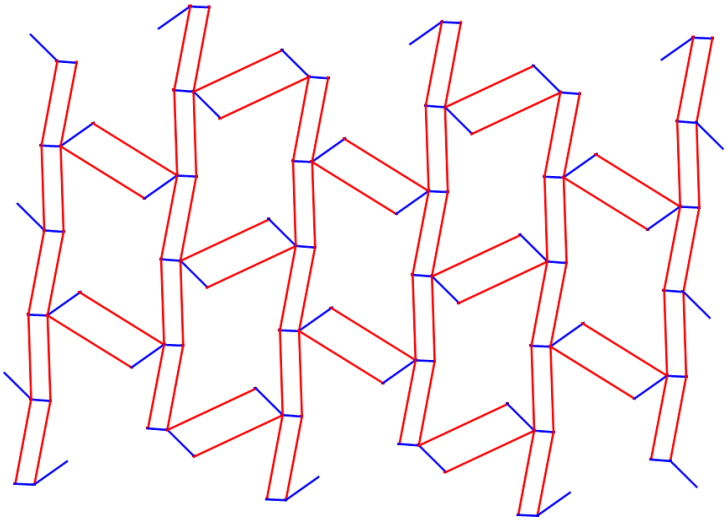
The separation distance measured between the two symmetrically independent silver atoms Ag1 and Ag2 is 6.439 Å, which could be viewed as the separation distance; if the ligand uses only the triazine nitrogen atoms of the ligand. The separation distance between Ag1 and Ag2' (7.220 Å) is shorter than the Ag1···Ag2" separation distance (12.956 Å). Ag1 is also bridged with Ag1' by one of the allyloxy arms of the ligand, and the Ag1···Ag1' separation distance is 10.539 Å. Ag2 has the same separation distance with its symmetrically related Ag2' and Ag2" (10.314 Å), which is similar to the Ag1···Ag1' separation distance. Considering the three allyloxy arms of the ligand as bridges, the separation distances of Ag1'···Ag2", Ag1'···Ag2' and Ag2'···Ag2" are 10.075 Å, 17.504 Å and 19.524 Å, respectively.

Within the rectangles formed in each direction of the complex around the triazine ring, one can see the phenyl rings position for π-π interactions with a separation distance of 3.650 Å between the centroids of the phenyl rings.[19, 154] The structure of the complex further grows into an oval shaped cavity, which is surrounded by the rectangular shaped assemblies, as shown in Figure 2.44A.

Considering the silver atom (Ag2) connected with three ligands and each ligand connected with five different silver atoms as nodes, a 2D network system was found, as shown in Figure 2.44B. The topology of silver could be expressed as $4^1.8^2$ and the ligand as $4^3.8^2$ network system.



A)



B)

Figure 2.44 *– A) The extended 2D structure of complex* ***2.50****, showing the oval shaped cavities. B) The simple representation of the 2D network system of complex* ***2.50****.*

2.5 Ligands containing four and six allyloxy groups

After studying the coordination chemistry of ligands containing one to three allyloxy groups with different silver(I) salts, the next step was to investigate the coordination chemistry of multi-allyloxy armed ligands using the compounds shown in Figure 2.45. Symmetry was an important factor in designing ligands containing multiple allyloxy arms.

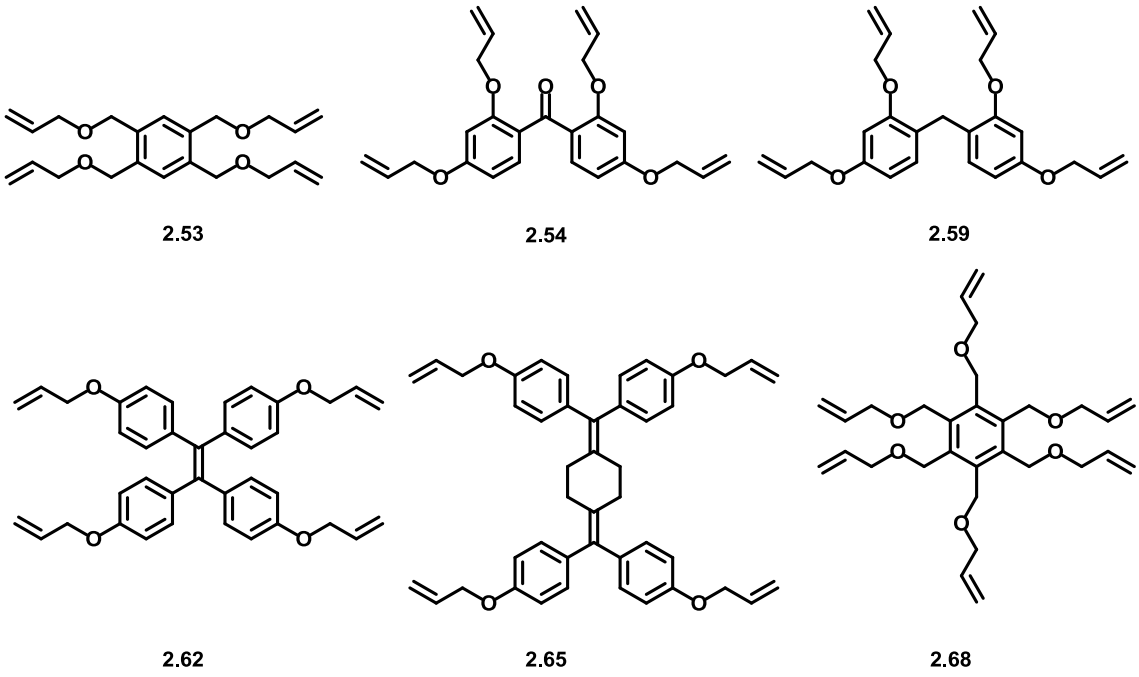


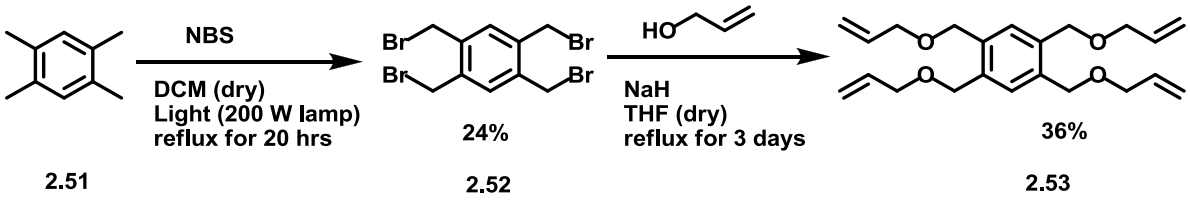
***Figure 2.45** – Compounds used to investigate the coordination of multi-allyloxy armed ligands with different silver(I) salts.*

2.5.1 Syntheses of ligands containing multi-allyloxy arms and their precursors

*2.5.1.1 Synthesis of 1,2,4,5-tetrakis(allyloxymethyl)benzene (**2.53**)*

Compound **2.53** was synthesised from the commercially available 1,2,4,5-tetramethylbenzene (durene) **2.51** in two steps, as shown in scheme 2.8. The first step was synthesising precursor **2.52** from durene by using a literature method.[155] 1,2,4,5-Tetrakis(bromomethyl)benzene (**2.52**) is a common precursor for making compounds with four donating groups for different applications.[156-157] The second step is another common method used in this project for attaching allyloxy arms with bromomethylarene compounds.[151]

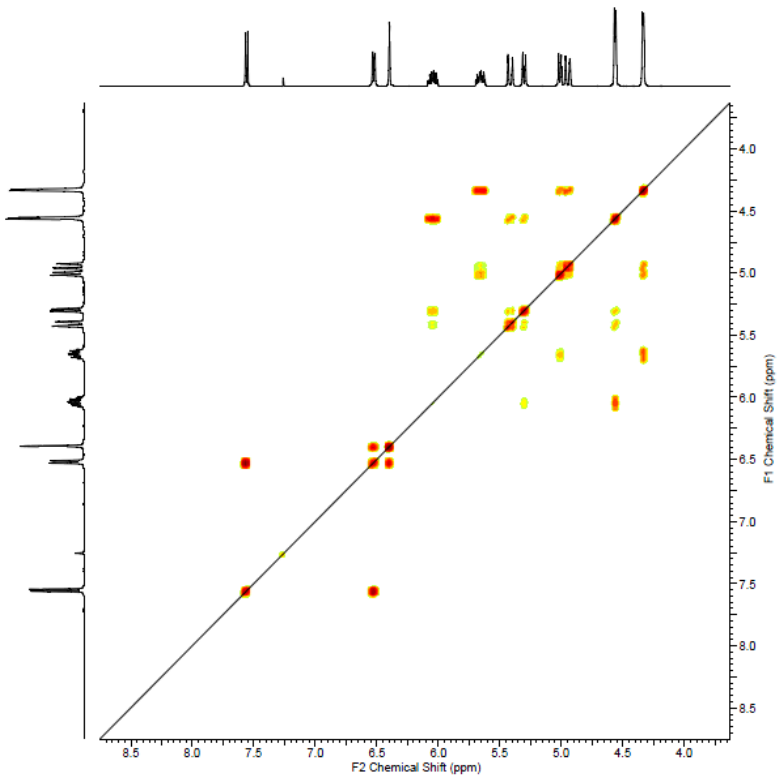
Compound **2.53** was reported in 1964 by German researchers,[158] but the paper was not accessible; therefore, **2.53** was characterised by ^{1}H NMR, ^{13}C NMR, mass and infrared spectra.



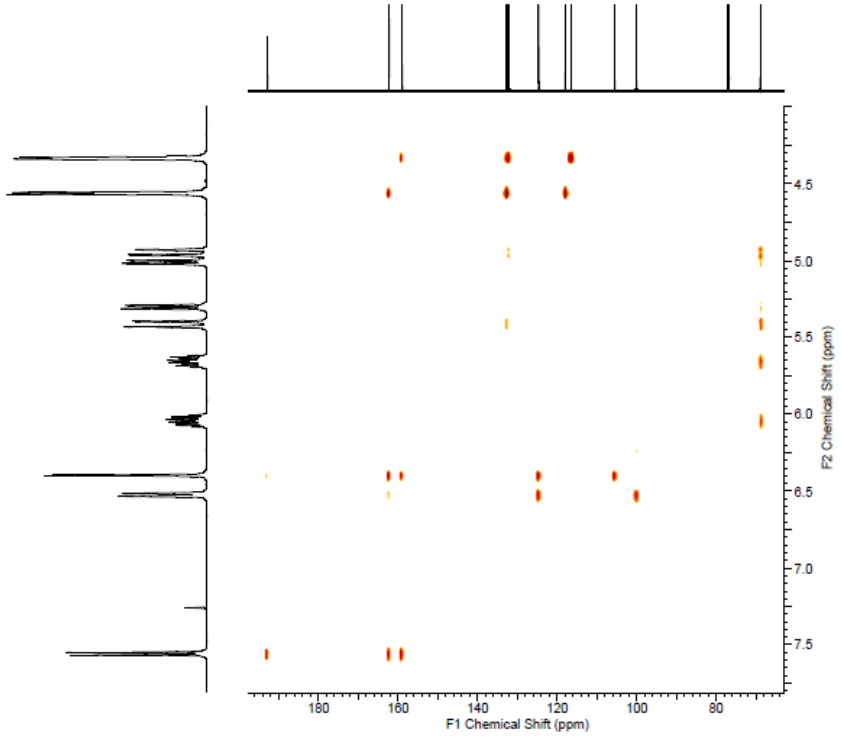
Scheme 2.8 *– The synthesis of ligand **2.53** from precursor **2.52** and allyl alcohol.*

*2.5.1.2 Synthesis of 2,2',4,4'-tetraallyloxybenzophenone (**2.54**)*

Compound **2.54** was synthesised from 2,2',4,4'-tetrahydroxybenzophenone under the conditions shown in scheme 2.1. Since **2.54** is a new compound, it was fully characterised using different techniques. The allyloxy arms in **2.54** are in two different environments, the assignment of the ^{1}H NMR and ^{13}C NMR were assisted by COSY and HMBC, as shown in Figure 2.46.



A)



B)

Figure 2.46 *–A) 2D ^{1}H NMR (COSY) of compound* ***2.54*** *B) 2D HMBC of compound* ***2.54****.*

Recrystallization of compound **2.54** from absolute alcohol gave crystals suitable for single crystal structure analysis; therefore, **2.54** was further characterised by an X-ray crystal structure. The structure was solved in the monoclinic $P2_1/c$ space group, in which the asymmetric unit contains a full molecule with one of the allyloxy arms disordered over two sites, as shown in Figure 2.47. The dominant site occupancy for the disordered allyloxy arm is 58%. The structure showed a twist at the carbonyl carbon between the two aryl rings.

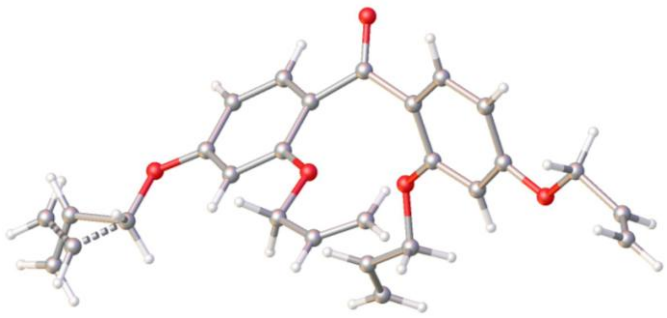
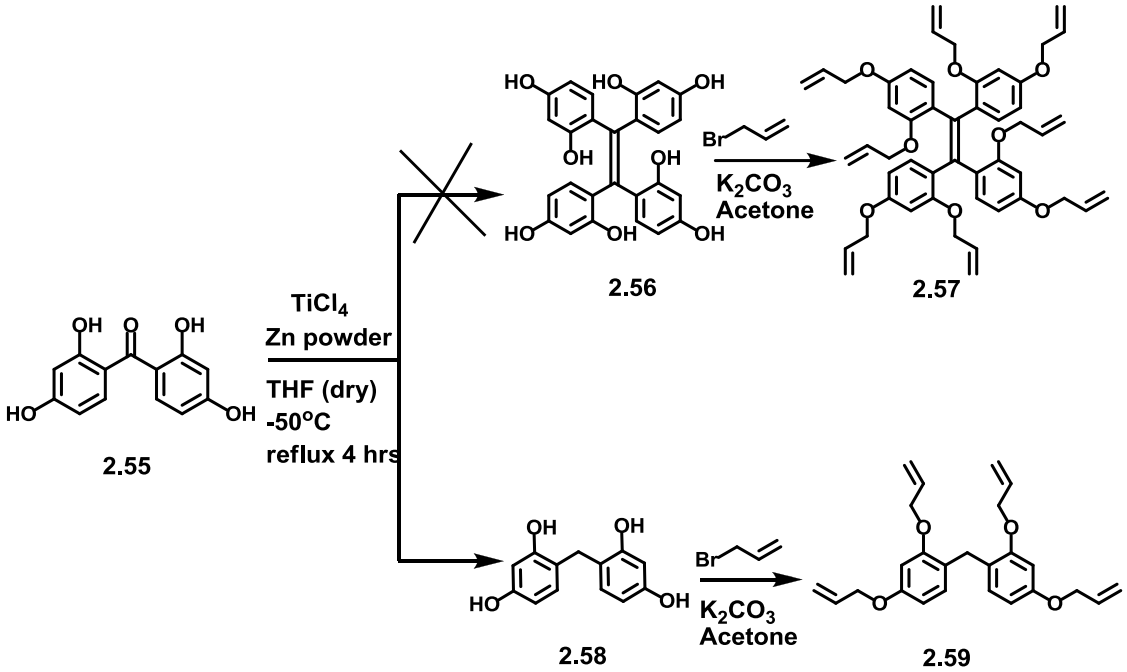


Figure 2.47 *– The structure of compound* ***2.54****. The disordered allyloxy arm is shown with broken bonds.*

*2.5.1.3 Synthesis of bis(2,4-diallyloxyphenyl)methane (**2.59**)*

Ligand **2.59** was obtained serendipitously during an attempt to synthesise 1,1,2,2-tetrakis(2,4-diallyloxyphenyl)ethene (**2.57**) from 2,2',4,4'-tetrahydroxybenzophenone (**2.55**) using a McMurry coupling[148] to make compound **2.56** and subsequent allylation reaction[142] to give **2.57**, as shown in scheme 2.9. However, instead of the McMurry coupling a Clemenson-type reduction leads to the formation of compound **2.58** and a subsequent allylation reaction gave **2.59**. Compound **2.59** is a new compound and was characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, mass and IR spectra.



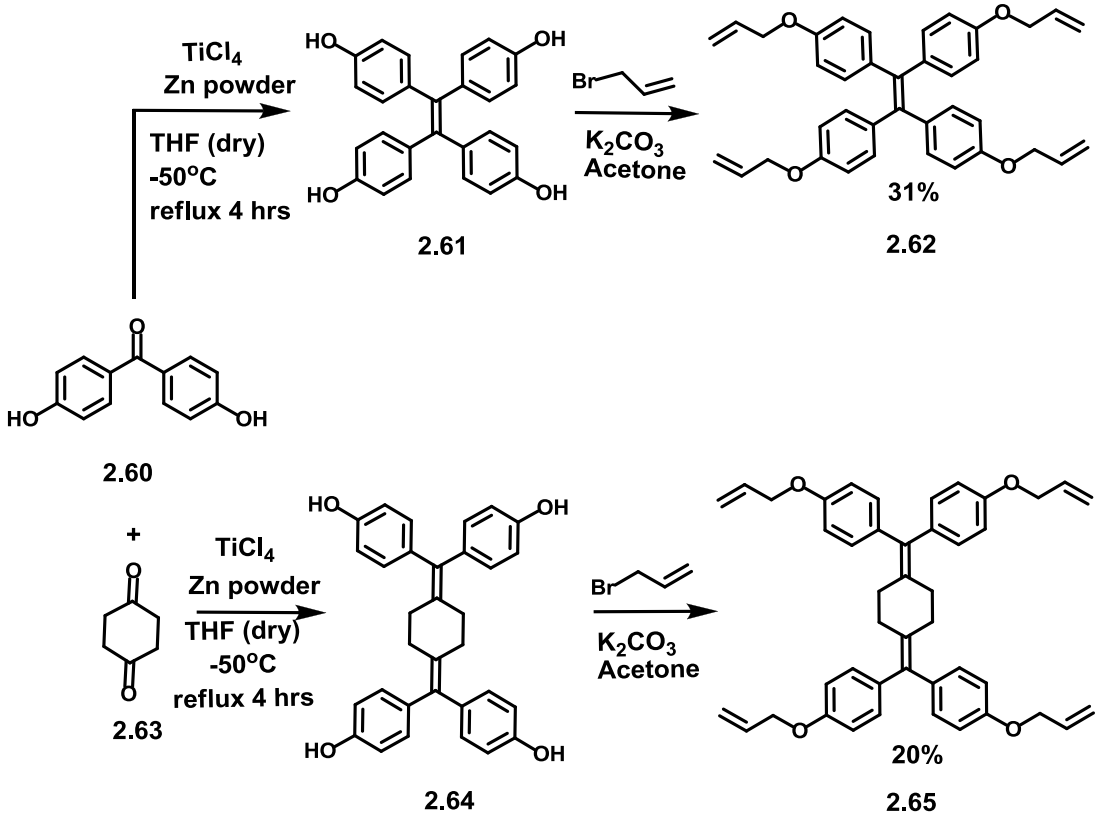
***Scheme 2.9** – An attempted synthesis of compound **2.57** and the serendipitously obtained compound **2.59**.*

*2.5.1.4 Syntheses of 1,1,2,2-tetrakis(4-allyloxyphenyl)ethene (**2.62**) and 1,4-bis(bis(4-allyloxyphenyl)methyledene)cyclohexane (**2.65**)*

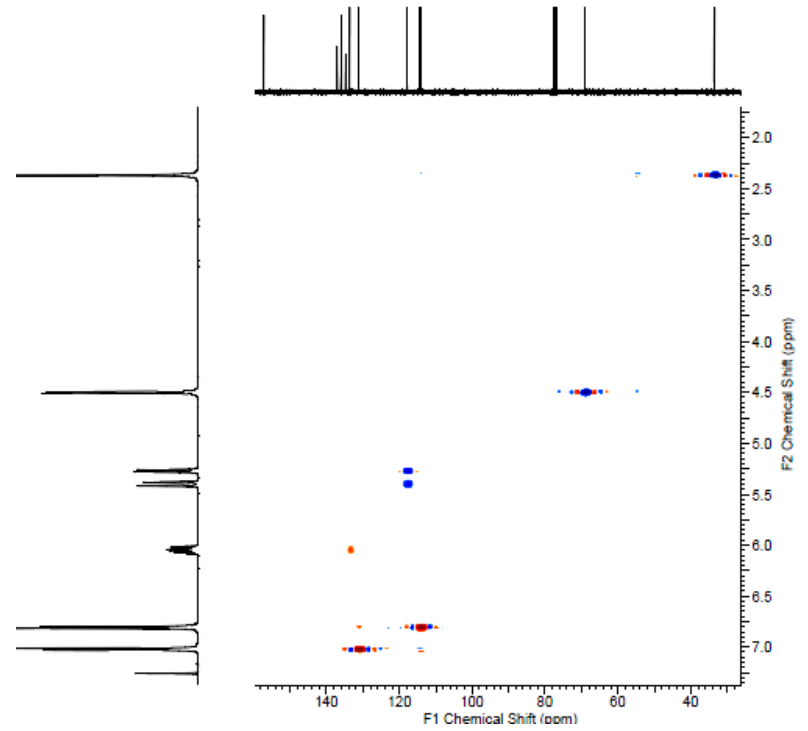
Compounds **2.62** and **2.65** were synthesized from their respective precursors by using the McMurry coupling reaction[148] followed by allylation,[142] as shown in scheme 2.10. In both reactions, the precursors **2.61** and **2.64** were not isolated due to the presence of mixtures of different products as well as the starting material that made purification by column chromatography difficult. Without purification of the intermediate products the next step was carried out

by adding excess allyl bromide. Since the products of the last step are non-polar, purification was much easier with column chromatography. Both **2.62** and **2.65** are new compounds, and were fully characterized by using the common characterization methods, including X-ray crystal structures. The assignment of ^{13}C NMR for **2.65** was supported by 2D HSQC and HMBC, as shown in Figure 2.48.

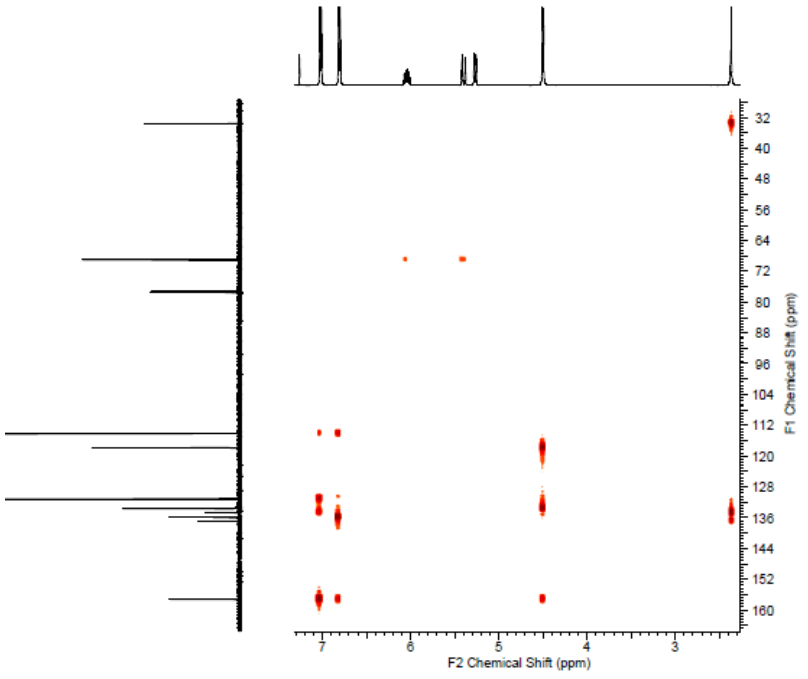
The structure of compound **2.62** was solved in the monoclinic $P2_1/n$ space group and the asymmetric unit contains one full molecule, as shown in Figure 2.49A. The structure of compound **2.65** was also solved in the $P2_1/n$ space group, in which the asymmetric unit contains half a molecule. The structure of **2.65** is shown in Figure 2.49B.



Scheme 2.10 *– Syntheses of compounds* ***2.62*** *and* ***2.65*** *and their respective precursors from compound* ***2.60****.*

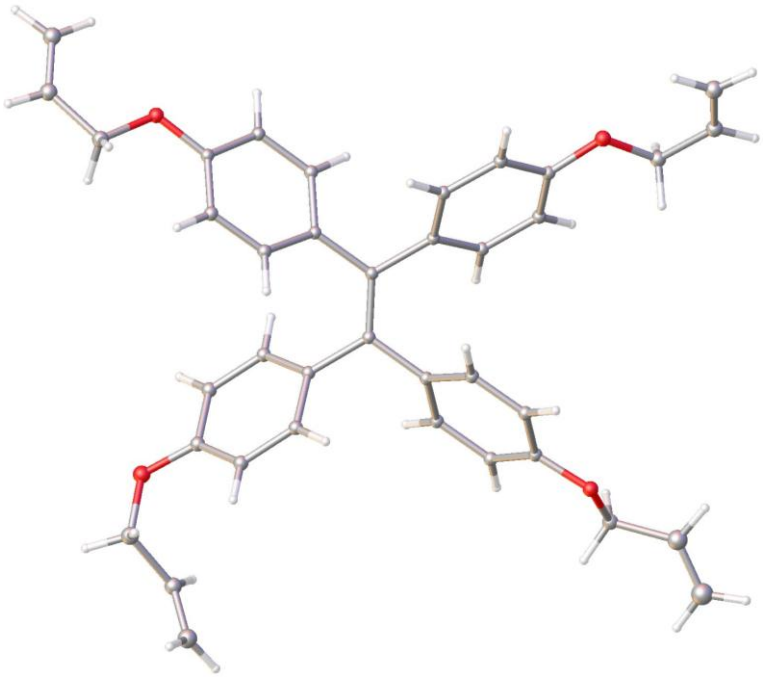


A)

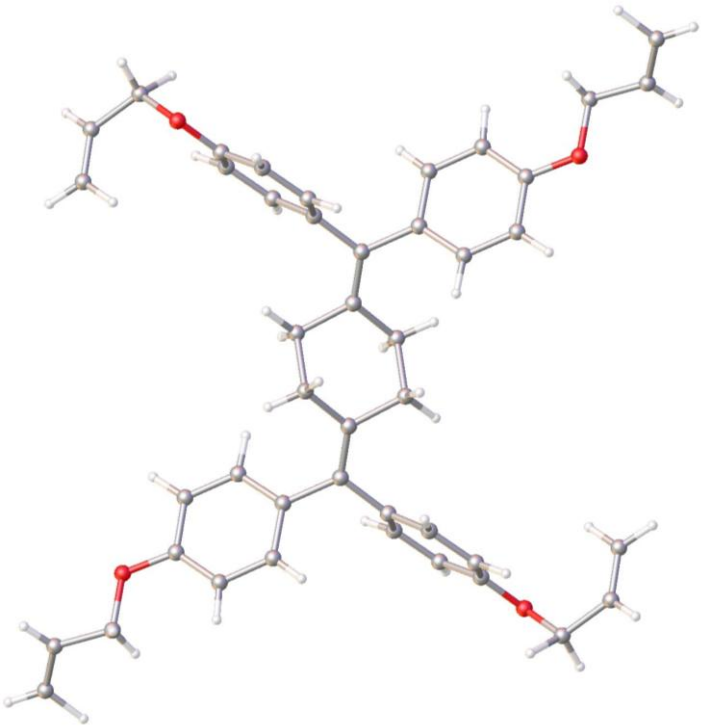


B)

Figure 2.48 *- A) 2D ^{1}H NMR (HSQC) of compound* ***2.65*** *B) 2D HMBC of compound* ***2.65****.*



A)

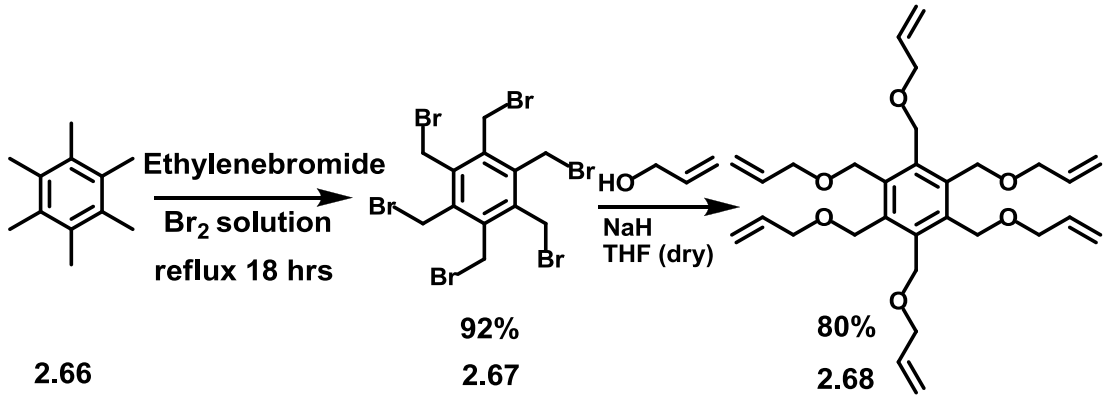


B)

Figure 2.49 *– A) The structure of compound* ***2.62****. B) The full structure of compound* ***2.65****.*

*2.5.1.5 The synthesis of 1,2,3,4,5,6-hexakis(allyloxymethyl)benzene (**2.68**)*

Ligand **2.68** was synthesised in two steps from the commercially available hexamethylbenzene (**2.66**) using a literature method[159] to make **2.67** followed by allylation using the commonly used method,[151] as shown in scheme 2.11. Precursor **2.67** is known for making different compounds that have six arms or linkages.[160-161] Compound **2.68** is a yellow oily liquid which has not been reported before, and was fully characterised by using NMR, elemental analysis, mass and IR spectra.



***Scheme 2.11** – Synthesis of compound **2.68** and precursor **2.67** from commercially available compound **2.66**.*

*2.5.2 Attempts to grow crystals of complexes of 1,2,4,5-tetrakis(allyloxymethyl)benzene (**2.53**) with different silver(I) salts*

Several attempts were made to grow crystals of complexes of **2.53** with different silver(I) salts by using different crystal growing methods from the usual diethyl ether diffusion into the reaction mixture, slow diffusion of the solvent to using H-tube and U-tube; however, no success was achieved.

*2.5.3 Complexes of 2,2',4,4'-tetraallyloxybenzophenone (**2.54**)*

<u>With silver(I) perchlorate (**2.69**)</u>

A solution of ligand **2.54** in acetone was added to four equivalents of silver(I) perchlorate solution in acetone. As soon as the solution of **2.54** was mixed with the silver(I) perchlorate solution a white precipitate formed. The white precipitate was dissolved in water and left for slow evaporation over a week.

Crystals were grown at the top of the water layer and a single crystal was mounted on the diffractometer for crystal structure analysis. The structure of the complex was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand molecule, two silver atoms, one coordinated perchlorate anion, one non-coordinated perchlorate anion and a coordinated water molecule, revealing a 1:2(ligand:metal) ratio or an M_2L_1 type coordination complex, as shown in Figure 2.50.

The overall structure of the complex is a discrete bimetallic assembly that involves the interaction of all the allyloxy arms, η^1-type interaction with one of the aromatic rings, and the silver atom that is not interacting with the aromatic ring is bonded to a water molecule.

Ag1 is four coordinate from two allyloxy arms of the ligand, perchlorate oxygen atom of the anion, and η^1-type interaction from the aromatic ring. Ag2 is three coordinate, two from the olefins of the allyloxy groups of the ligand and a water molecule instead of the perchlorate anion.

The interesting feature of the structure is the way the allyloxy arms interact with silver atoms. Each allyloxy arm that interacts with the silver comes from the adjacent aryl rings, no two allyloxy arms from the same aromatic ring of the ligand are coordinated with the same silver atom, as shown in Figure 2.50.

Interestingly, no coordination of the carbonyl oxygen of the ligand was observed unlike the case of complex **2.33**, in which the carbonyl oxygen of the ligand (**2.21**) coordinates with silver.

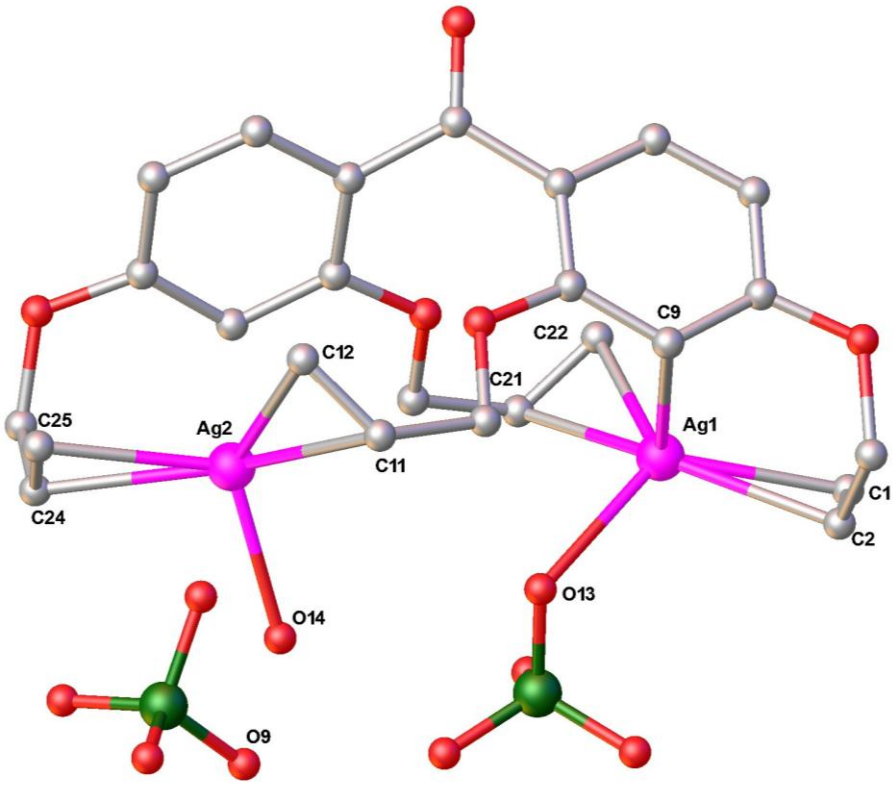


Figure 2.50 *– The binuclear discrete assembly of complex* ***2.69****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C1 2.375(4), Ag1-C2 2.486(4), Ag1-C1,C2 2.340(4), Ag1-C9 2.692(4), Ag1-C21 2.443(4), Ag1-C22 2.358(4), Ag1-C21,C22 2.307(4), Ag1-O13 2.403(3),C9-Ag1-O13 91.3(2), C9-Ag1-C1,C2 91.7(1), C9-Ag1-C21,C22 113.7(1), O13-Ag1-C1,C2 112.0(1), O13-Ag1-C21,C22 104.7(1), C1,C2-Ag1-C21,C22 134.6(2), Ag2-C11 2.453(4), Ag2-C12 2.363(4), Ag2-C11,C12 2.313(4), Ag2-C24 2.532(4), Ag2-C25 2.431(4), Ag2-C24,C25 2.392(4), Ag2-O14 2.286(3), O14-Ag2-C11,C12 113.3(1), O14-Ag2-C24,C25 103.8(2), C11,C12-Ag2-C24,C25 128.7(1).*

As shown in Figure 2.50, the structure of the complex has a twist at the carbonyl carbon junction. Moreover, the interaction of the olefins from adjacent aromatic groups with silver atoms positions one of the phenyl rings closer to the Ag1 environment, which results in a long range Ag1-C9 interaction, while the second phenyl ring is far from the Ag2 environment.

One of the oxygen atoms of the non-coordinated perchlorate anion has a hydrogen bond with the coordinated water molecule.

Ag1 is four coordinate with the biggest bond angle 134.6°, measured between the centroids of the olefins (C1=C2 and C21=C22). The second largest bond angle around the environment of Ag1 is 113.7°, and is measured between the η^1-type coordinated carbon atom (C9) of the aromatic ring and the centroid of the olefin (C21=C22). The third largest bond angle is measured between the oxygen atom of the perchlorate anion (O13) and the centroid of C1=C2 with a bond angle of 112.0°. From the measured bond angles, the calculated τ_4 value for Ag1 is 0.79, revealing a seesaw shape.

Ag2 is three coordinate through the coordination of two olefins (C11=C12 and C24=C25) and one water molecule with bond angles (C11,C12-Ag2-C24,C25 128.7°, O14-Ag2-C11,C12 113.3° and O14-Ag2-C24,C25 128.7°). From the measured bond angles Ag2 has a distorted trigonal planar shape.

The ligand doubly bridges the two silver atoms (Ag1⋯Ag2) with a separation distance of 5.964 Å. Even though the ligand bridges the two silver atoms, **2.54** acts as a bichelating tetradentate ligand, where two donor groups of the ligand coordinates with a single metal atom.

With silver(I) triflate (**2.70**)

A solution of ligand **2.54** in acetone was mixed with four equivalents of silver(I) triflate in acetone. Diethyl ether diffusion into the reaction mixture for a week resulted in a colourless gummy material. The gummy material was dissolved in a mixture of xylene and acetone and diethyl ether diffusion into the solution for another week resulted in the growth of colourless crystals. The structure of the complex was solved in the triclinic P-1 space group. The asymmetric unit contains one full ligand molecule, two silver atoms, one coordinated triflate anion and one non-coordinated triflate anion, as shown in Figure 2.51.

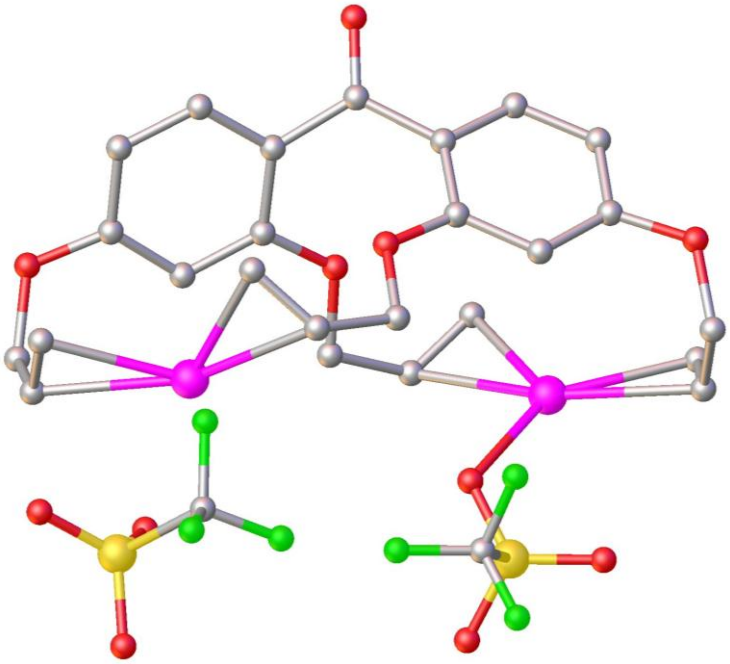


Figure 2.51 *– The asymmetric unit of complex* ***2.70****. All hydrogen atoms have been omitted for clarity.*

The asymmetric unit of complex **2.70** is similar to that of complex **2.69**. However, the full structure of complex **2.70** grows into tetranuclear dimeric discrete assembly or an M_4L_2 type coordination complex. The growth of the structure into a dimeric discrete assembly is a result of the different anion. In complex **2.69**, the perchlorate anion bonded in a monodentate terminating type of coordination, while the triflate counter anion bridges adjacent silver atoms, as shown in Figure 2.52. The other difference between the structures of complex **2.69** and **2.70** is the η^1-type interaction of the aromatic ring with silver in complex **2.69**, which is not observed in **2.70**.

No two olefins from the same aryl group bonded with a single silver atom, rather two allyloxy arms from adjacent aromatic rings interact with each silver atom. This resulted in an Ag1····Ag2 separation distance of 6.348 Å. However, ligand **2.54** could also be taken as a bichelating tetradentate ligand since two donor sites of the ligand are coordinating with the same metal atom. The triflate counter anion acts as a bidentate bridging ligand that leads to a capping of the complex structure into a tetranuclear discrete assembly. The Ag·····Ag separation distance measured between Ag1 and Ag2’ due to the

bridging triflate anion is 5.457 Å, which is shorter than the Ag1⋯Ag2 separation distance measured due to the doubly bridging allyloxy arms of the ligand.

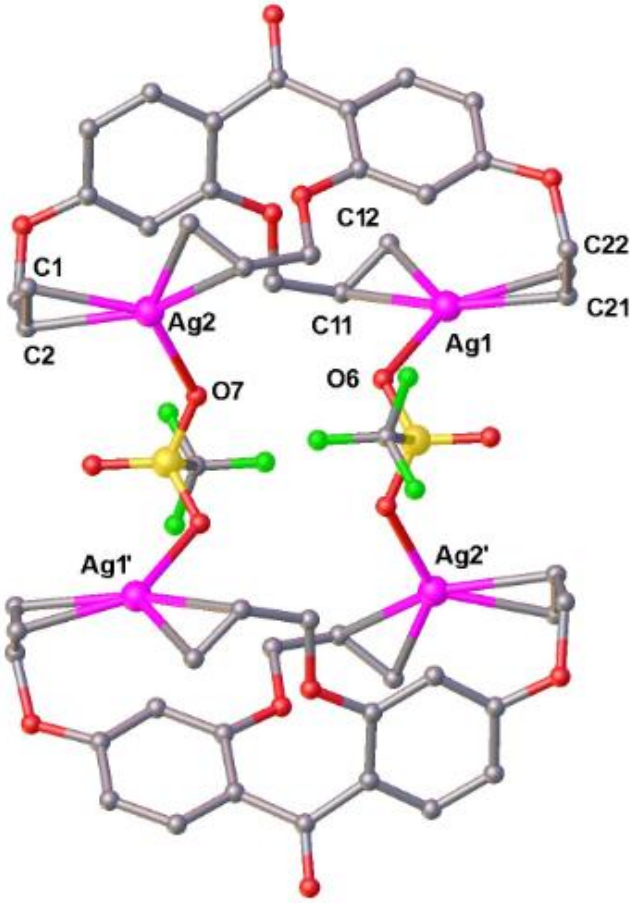


Figure 2.52 *– The M_4L_2 type tetranuclear discrete assembly of complex* ***2.70****. All hydrogen atoms and the non-coordinated triflate anions are excluded for clarity. Selected bond lengths (Å) and angles (°): Ag1-C11 2.517(3), Ag1-C12 2.398(2), Ag1-C11,C12 2.367(3), Ag1-C21 2.496(3), Ag1-C22 2.401(3), Ag1-C21,C22 2.355(3), Ag1-O6 2.315(2), O6-Ag1-C11,C12 104.9(1), O6-Ag1-C21,C22 123.2(1), C11,C12-Ag1-C21,C22 132.2(1), Ag2-C1 2.401(3), Ag2-C2 2.478(3), Ag2-C1,C2 2.347(3), Ag2-C24 2.427(3), Ag2-C25 2.348(3), Ag2-C24,C25 2.293(3), Ag2-O7 2.299(2), O7-Ag2-C1,C2 111.5(1), O7-Ag2-C24,C25 122.1(1), C1,C2-Ag2-C24,C25 126.7(1).*

As shown in Figure 2.52, each silver atom is three coordinate through the interaction of two olefin groups and an oxygen atom from the triflate anion. The bond angles around the environment of Ag1 are 132.1°, 123.1° and 104.8°, which shows Ag1 has a distorted trigonal planar shape. The bond angles around Ag2 are 126.6°, 122.0° and 111.4°, which are closer to the ideal trigonal planar geometry angle (120.0°).

*2.5.4 Complex of bis(2,4-diallyloxyphenyl)methane (**2.59**)*

With silver(I) perchlorate (**2.71**)

A solution of **2.59** in acetone reacted with four equivalents of silver(I) perchlorate and diethyl ether diffusion into the reaction vial resulted in the growth of crystals suitable for single crystal structure analysis. The structure solved in the triclinic P-1 space group. The structure is a discrete assembly formed from one full ligand molecule, two silver atoms, one coordinated perchlorate anion and a non-coordinated perchlorate anion, as shown in Figure 2.53.

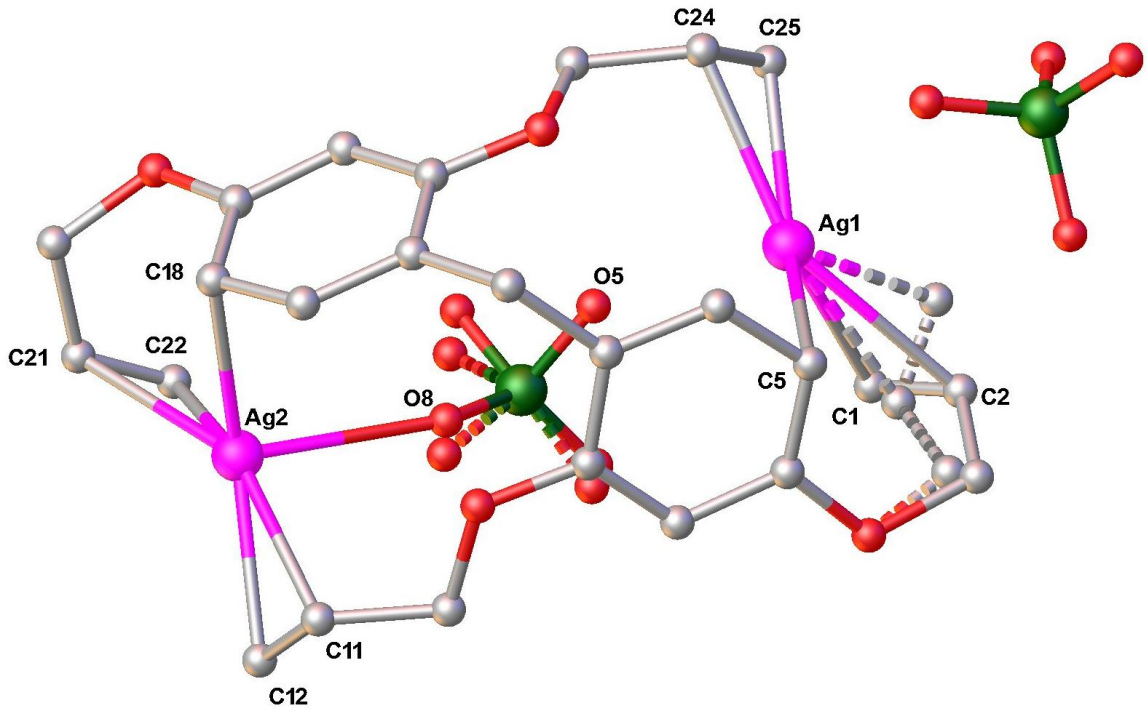


***Figure 2.53** – The discrete structure of complex **2.71**. The disorder in the coordinated perchlorate anion and one of the*

allyloxy arms is represented by broken lines. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-C1 2.493(3), Ag1-C2 2.703(3), Ag1-C1,C2 2.514(3), Ag1-C5 2.414(2), Ag1-C24 2.448(2), Ag1-C25 2.349(2), Ag1-C24,C25 2.303(2), C5-Ag1-C1,C2 88.5(1), C5-Ag1-C24,C25 136.6(1), C1,C2-Ag1-C24,C25 132.1(1), Ag2-C11 2.433(2), Ag2-C12 2.369(2), Ag2-C11,C12 2.306(2), Ag2-C18 2.417(2), Ag2-C21 2.630(2), Ag2-C22 2.470(2), Ag2-C21,C22 2.463(2), Ag2-O8 2.579(2), C18-Ag2-O8 99.1(2), C18-Ag2-C11,C12 129.1(1), C18-Ag2-C21,C22 90.3(2), O8-Ag2-C11,C12 90.7(4), O8-Ag2-C21,C22 99.2(1), C11,C12-Ag2-C21,C22 137.5(1).

As shown in Figure 2.53, one of the allyloxy arms and one of the perchlorate anions have disorder over two sites with 73% and 57% dominant site occupancies, respectively. The minor site occupancies of the disorder are shown with broken bonds.

Ag1 is three coordinate through the interaction of two olefins and one η^1-type interaction from the aromatic ring. The largest and smallest bond angles around Ag1 are measured between C5 and the centroids of C24=C25 and C1=C2 with bond angles of 136.5° and 88.4° respectively. The other bond angle is between the centroids of the olefins (C1=C2 and C24=C25) with a bond angle of 132.0°, revealing a highly distorted trigonal geometry.

The silver-carbon interactions from the centroid of the olefin groups as well as the η^1-type interaction of the aromatic ring are within the expected range except that the individual Ag1-C2 bond length (2.703 Å) is longer than the silver-carbon bond lengths measured elsewhere in this project. The long distance of Ag1-C2 may be due to the disorder observed but the silver-carbon bond distances with the minor contributor are in the usual range.

Ag2 is four coordinate through the interaction of two olefins, one η^1-type interaction from the second aromatic ring of the ligand and an oxygen atom of the perchlorate anion. The largest bond angle around the environment of Ag2

is measured between the centroids of the olefins with a value of 137.4°. The calculated τ_4 value for Ag2 is 0.66, revealing a seesaw geometry.

The Ag2-carbon bond lengths from the centroid of the olefins as well as the η^1-type interaction from the aromatic ring are in the expected bond length range for such types of interactions. In both Ag1 and Ag2, the silver-carbon bond lengths for η^1-type interaction from the aromatic ring (2.414 Å and 2.417 Å) are shorter than the bond length for the similar interaction in complex **2.69**.

The Ag2-O8 bond length (2.579 Å) is also within the expected range for silver-oxygen interactions but longer than most of the silver-oxygen bond lengths measured elsewhere in this project. The closest oxygen atom around the Ag1 environment is O5 with a separation distance of 2.636 Å, which is a long weak interaction.

Ligands **2.54** and **2.59** are very similar, as are their respective complexes **2.69** and **2.71**, except for some minor differences as outlined in the above paragraphs.

*2.5.5 Complexes of 1,1,2,2-tetrakis(4-allyloxyphenyl)ethene (**2.62**)*

With silver(I) perchlorate (**2.72**)

A solution of ligand **2.62** in acetone was mixed with five equivalents of silver(I) perchlorate solution in acetone. Slow evaporation of the solvent over two weeks afforded tiny crystals. Single crystal structure analysis revealed a cyclization around the aromatic ring, oxygen migration and a loss of an allyl group, as shown in Figure 2.54.

The structure of the complex solved in the P-1 space group and the asymmetric unit contains one rearranged ligand molecule, one and half silver atoms, a coordinated water molecule and one and half non-coordinated perchlorate anions. The data were poor, as is the refinement (R_1=7.33%).

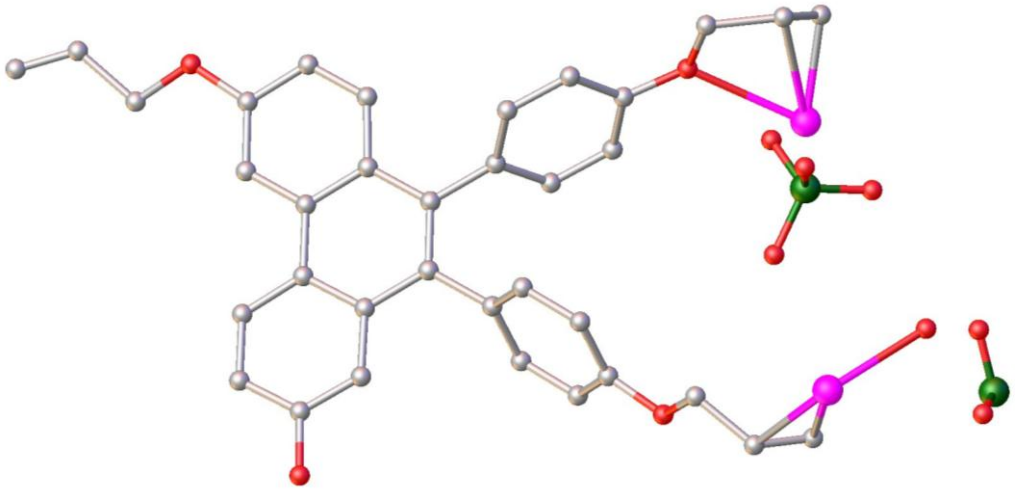


Figure 2.54 *– The asymmetric unit of complex* ***2.72****, showing the rearrangement of the ligand. All hydrogen atoms have been omitted.*

The overall structure of the complex is a 2D polymeric assembly that involves the interaction of the olefins as well as the oxygen atom of one allyloxy arm, as shown in Figure 2.55. Complex **2.72** not only has an unexpected ring cyclization to a phenanthrene, but also the interaction of the oxygen atom of one allyloxy arm with silver is the first such observation in this project. Burgess reported one structure that involves this type of interaction.[60]

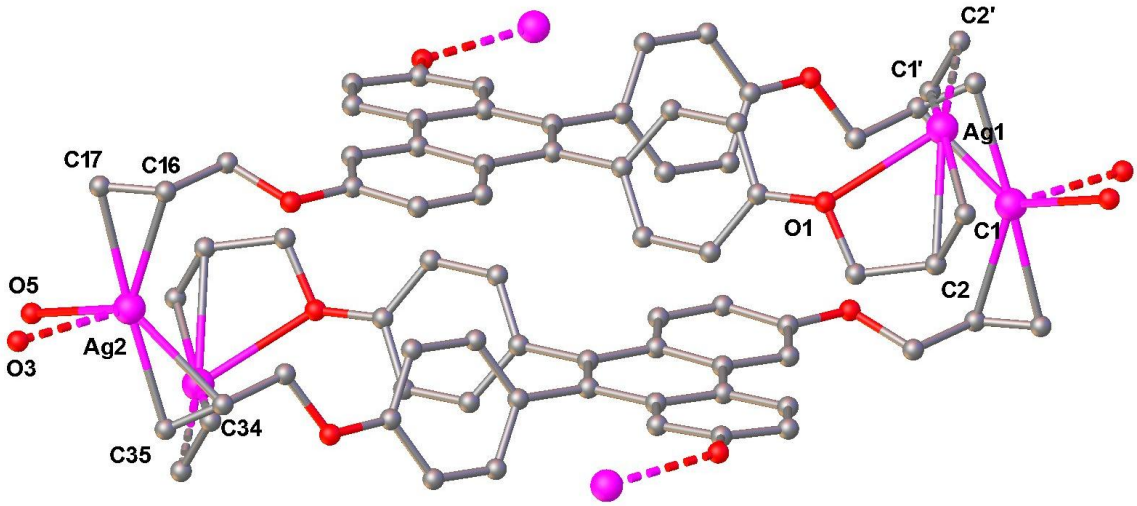


Figure 2.55 *– Part of the 2D polymeric assembly of complex* ***2.72****. All hydrogen atoms and the perchlorate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°):*

Ag1-C1 2.164(2), Ag1-C2 2.604(1), Ag1-C1,C2 2.307(2), Ag1-O1 2.573(2), Ag1-C1' 2.598(2), Ag1-C2' 2.418(1), Ag1-C1',C2' 2.426(2), O1-Ag1-C1,C2 61.5(4), O1-Ag1-C1',C2' 112.4(4), C1,C2-Ag1-C1',C2' 145.0(2), Ag2-C34 2.464(1), Ag2-C35 2.362(1), Ag2-C34,C35 2.332(1), Ag2-O5 2.347(2), Ag2-C16 2.439(2), Ag2-C17 2.387(1), Ag2-C16,C17 2.330(1), Ag2-O3 2.570(2), O5-Ag2-O3 74.6(2), O5-Ag2-C16,C17 106.1(3), O5-Ag2-C34,C35 106.9(4), O3-Ag2-C16,C17 92.9(3), O3-Ag2-C34,C35 105.2(3), C16,C17-Ag2-C34,C35 145.5(4).

Ag1 is three coordinate through the interactions of two olefins and an oxygen atom. The largest bond angle around the Ag1 environment is 145.0°, and is formed between the centroids of the olefins. The other two angles are 112.4° and 61.5°, revealing a highly distorted trigonal shape. All the silver-carbon separation distances between the centroid of the olefin and silver are in the expected range. Interestingly, the Ag1-O1 bond length (2.573 Å) from the interaction of the allyloxy arm of the ligand with silver is shorter than the sum of the ionic radii between silver and oxygen (2.66 Å).[110]

Ag2 is four coordinate from two olefins and two oxygen atoms. 145.5° is the largest bond angle measured around the environment of Ag2, which is formed between the centroids of the two olefins. The other two large bond angles are 106.9° and 106.1°, which are measured between the oxygen atom of the water molecule and the centroids of the olefins. The calculated τ_4 value for Ag2 is 0.76, revealing a seesaw shape.

As shown in Figure 2.55, the phenanthrene system formed from the cyclization process is flat, while the other two phenyl rings are twisted perpendicular to the plane of the phenanthrene ring. There is an edge-to-face π-π interaction between the edge of the phenyl ring from the top layer and the centroid of the corresponding phenyl rings of the phenanthrene from the bottom layer with separation distances of 3.613 Å and 3.664 Å.[20, 154]

The powder diffraction pattern showed a good agreement with the calculated one, as shown in Figure 2.55. This confirms that the product obtained is not only observed for a single crystal, but also for the whole sample.

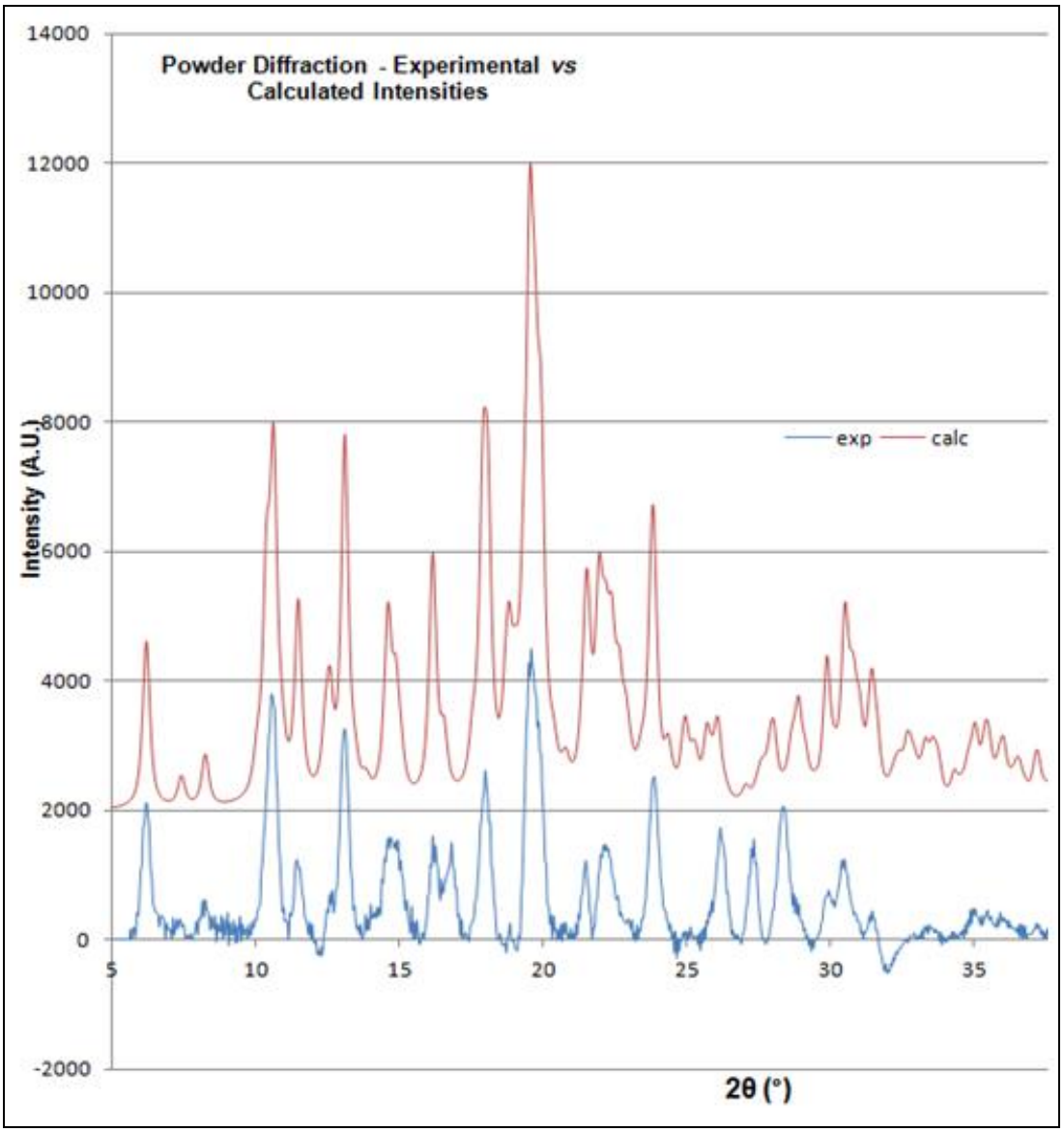


Figure 2.56 *– The powder diffraction of complex* ***2.72****, showing the experimental result in blue and the calculated one in red.*

The ^{1}H NMR also supported the formation of the rearranged product as shown in Figure 2.57. The assignment of the ^{1}H NMR was supported by a 2D COSY. Mass spectrometry and elemental analysis supported the formation of the rearranged product.

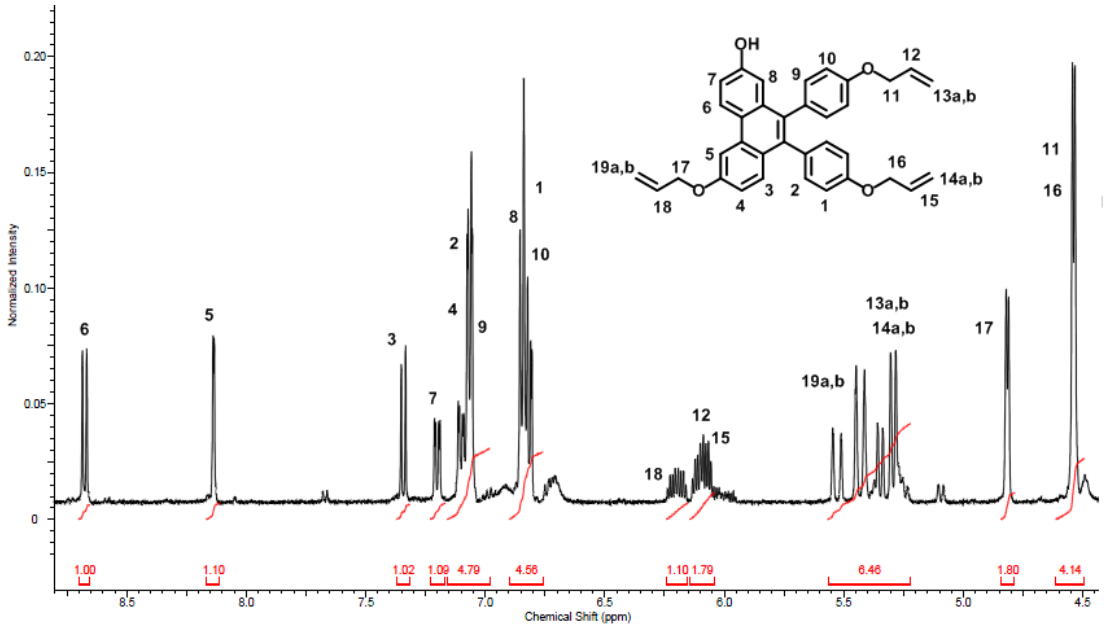
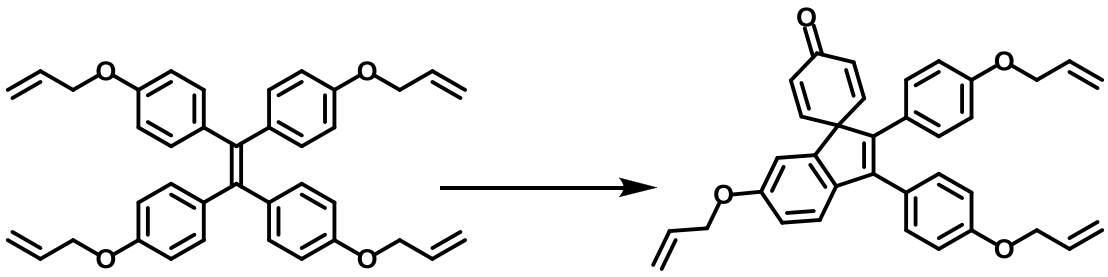


Figure 2.57 *– The ^{1}H NMR of complex* ***2.72*** *in acetonitrile.*

Only one compound has been reported with this carbon skeleton and oxygenation pattern as a minor product in a palladium catalysed coupling reaction.[162] The rearrangement probably proceeds via the intermediate dienone (**2.62A**), shown in scheme 2.12. Such spirodienones are readily formed by metal catalysed rearrangement of 1,2-bis(4-alkoxyphenyl) – precursors[163-164] and readily undergo dienone – phenol rearrangements to phenanthrenes[165-166] with selective migration of the alkenyl group.[166]



2.62 **2.62A**

Scheme 2.12 *– The probable rearrangement to intermediate dienone* ***2.62A****.*

Solution studies were attempted to investigate whether the cyclization to the phenanthrene happened first followed by the loss of the allyloxy arm or the

other way around. A solution of ligand **2.62** in deuterated acetonitrile (CD_3CN) was mixed with five equivalents of silver(I) perchlorate solution in deuterated acetonitrile (CD_3CN) and followed by ^1H NMR in 12 hours intervals; and during the second day crystals were observed inside the NMR vial.

A very small crystal was mounted on the diffractometer and the structure was solved in the monoclinic C2/c space group. The asymmetric unit contains half a ligand molecule, one acetonitrile, half a silver atom and half a perchlorate anion, as shown in Figure 2.58. Both the silver atom and perchlorate anion lie on a twofold rotation axis, and have half occupancy but for the sake of clarity the perchlorate anion is shown as a full anion in Figure 2.58.

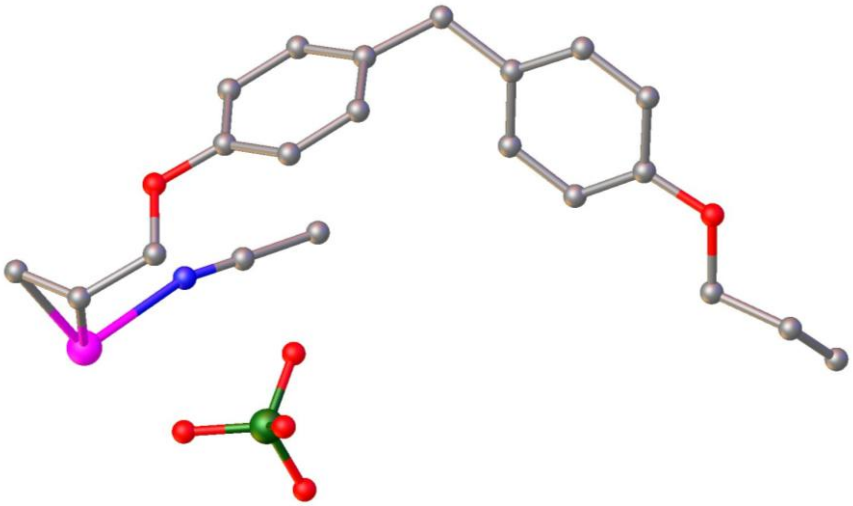


Figure 2.58 *– The asymmetric unit of complex of ligand* ***2.62*** *with silver(I) perchlorate in acetonitrile. All hydrogen atoms are excluded for clarity.*

As shown in Figure 2.59, the full structure of the complex is a 1D linear polymeric assembly, in which the ligand uses only two of the allyloxy arms for interaction with silver. The interacted allyloxy arms are in a cis-position relative to each other. Each silver atom is also bonded with two molecules of acetonitrile.

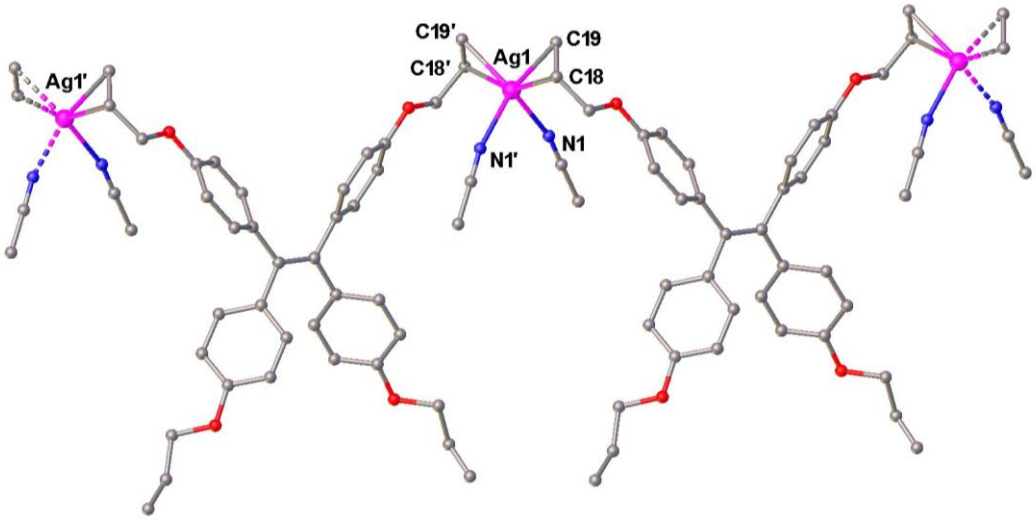


Figure 2.59 *– Part of the 1D polymeric assembly of the complex of ligand* ***2.62*** *and silver(I) perchlorate in acetonitrile. All hydrogen atoms and the perchlorate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C18 2.498(2), Ag1-C19 2.416(2), Ag1-C18,C19 2.366(2), Ag1-N1 2.311(2), N1-Ag1-N1' 87.4(4), N1-Ag1-C18,C19 110.3(3), N1-Ag1-C18',C19' 108.2(3), N1'-Ag1-C18,C19 108.2(3), N1'-Ag1-C18',C19' 110.3(3), C18,C19-Ag1-C18',C19' 125.7(3).*

The ligand acts in a bidentate bridging manner that connects adjacent silver atoms (Ag1····Ag1') with a separation distance of 14.329 Å. All the silver-carbon interactions as well as the silver-nitrogen interactions are in the expected range for each type of interaction.[60, 110, 132, 153]

With silver(I) triflate (**2.73**)

Crystals were grown from the reaction of five equivalents of silver(I) triflate in acetone and ligand **2.62** in nitromethane. However, the crystals were very small plates, which were not ideal for X-ray structure analysis. A single crystal was mounted on the diffractometer and the structure solved in the P2/c space group. The data was not good, consequently the refinement (R_1=18.0%) is very poor and to make matters worse all the triflate anions are disordered, which contributes towards the poor refinement value. The asymmetric unit

contains one and a half ligand molecules, four silver atoms, four triflate anions and three water molecules, as shown in Figure 2.60.

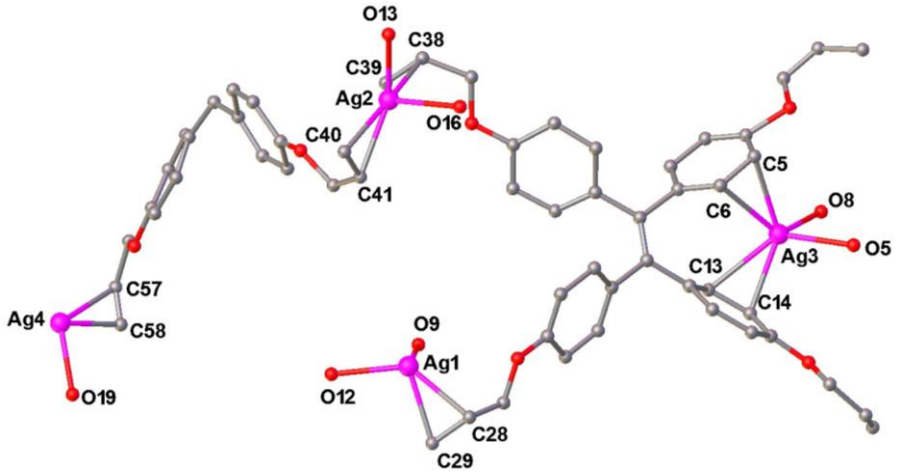


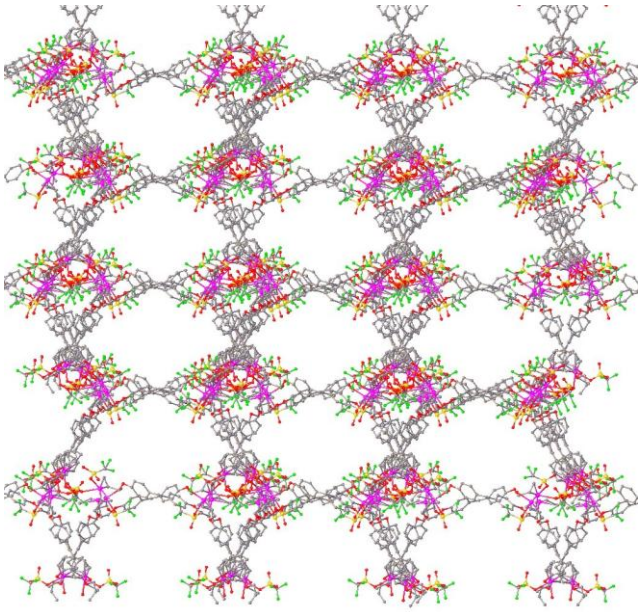
Figure 2.60 *– The asymmetric unit of complex* ***2.73****. All hydrogen atoms and part of the triflate counter anions except the bonded oxygen atoms are omitted. Selected bond lengths (Å) and angles (°): Ag1-C28 2.346(1), Ag1-C29 2.374(1), Ag1-C28,C29 2.259(1), Ag1-O25 2.312(9), Ag1-O9 2.506(1), O25-Ag1-O9 90.3(2), O25-Ag1-C28,C29 117.4(4), O9-Ag1-C28,C29 99.5(4), Ag2-C40 2.380(1), Ag2-C41 2.329(1), Ag2-C38 2.444(1), Ag2-C39 2.428(2), Ag2-C38,C39 2.341(2), Ag2-C40,C41 2.257(1), Ag2-O13 2.310(2), Ag2-O16 2.493(1), O13-Ag2-O16 77.9(1), O13-Ag2-C38,C39 99.9(2), O13-Ag2-C40,C41 122.2(2), O16-Ag2-C38,C39 112.426), O16-Ag2-C40,C41 98.4(2), C38,C39-Ag2-C40,C41 132.3(2), Ag3-C5 2.501(1), Ag3-C6 2.609(1), Ag3-C5,C6 2.453(1), Ag3-C13 2.612(1), Ag3-C14 2.477(1), Ag3-C13,C14 2.444(1), Ag3-O5 2.311(1), Ag3-O8 2.375(2), O5-Ag3-O8 81.4(4), O5-Ag3-C5,C6 115.5(2), O5-Ag3-C13,C14 115.7(3), O8-Ag3-C5,C6 113.0(2), O8-Ag3- C13,C14 121.6(2), C5,C6-Ag3-C13,C14 107.9(4), Ag4-O19 2.255(2), Ag4-C57 2.592(2), Ag4-C58 2.194(2), Ag4-C57,C58 2.332(2), O19-Ag4-C57,C58 107.5(2).*

All four of the silver atoms are four coordinate, each with two η^2-type olefin or arene bonds and two oxygen atoms from the triflate anion and water

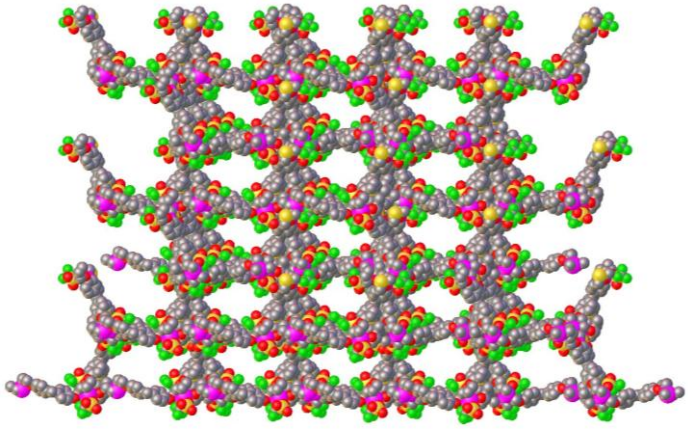
molecules. As shown in Figure 2.60, two of the phenyl rings of the ligand interact with Ag3 in a chelating manner. This interaction of the two phenyl rings with a single silver atom might give an idea how the cyclization and rearrangement of ligand **2.62** happened in complex **2.72**, but it needs more investigation with a convincing crystal structure refinement in order to be considered as good support for the mechanism of the rearrangement observed in complex **2.72**.

All the triflate anions and the water molecules are bonded with silver in a terminating manner. The ligand is chelating through the phenyl rings, while bridging through the four olefin groups of the allyloxy arms.

The overall structure of complex **2.73** is a 3D-polymeric assembly that involves the coordination of all four allyloxy arms and two of the olefin groups of the ligand as shown in Figure 2.61A. As shown in the space filling diagram of **2.73** (Figure 2.61B), the structure has large cavities; however, due to the poor refinement of the structure no further investigation was possible. Interestingly, complex **2.73** is the only 3D polymeric structure obtained throughout this project. A number of attempts were made to grow crystals of **2.73** using different methods in order to get a better quality crystal but all the attempts except the above one were not fruitful.



A)



B)

Figure 2.61 *– A) Part of the 3D polymeric structure of complex* ***2.73****. B) The space filliing diagram of complex* ***2.73****. All hydrogen atoms have been omiited for clarity.*

With silver(I) tetrafluoroborate (**2.74**)

Crystals were grown from the reaction of ligand **2.62** with four equivalents of silver(I) tetrafluoroborate solution in acetone. The structure of the complex was solved in the monoclinic $P2_1$ space group. The asymmetric unit contains two ligand molecules, four silver atoms, six coordinated and two non-coordinated water molecules, and four non-coordinated tetrafluoroborate anion, as shown in Figure 2.62.

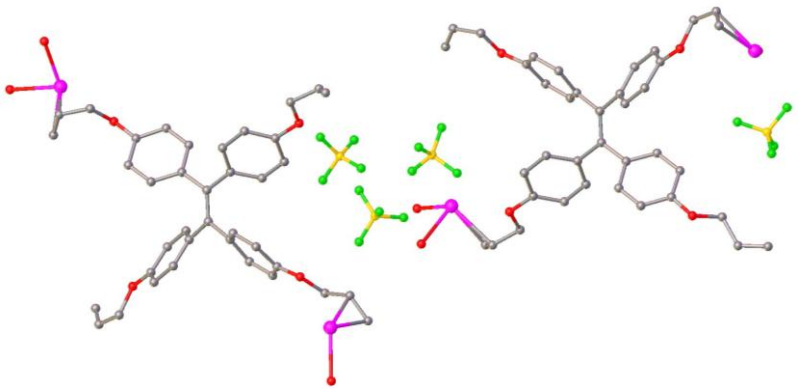
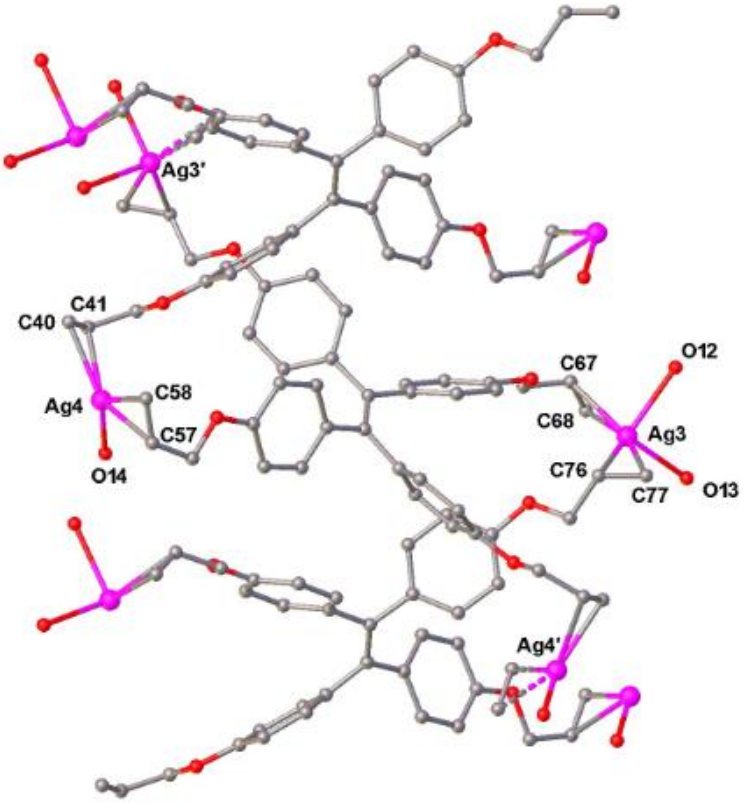


Figure 2.62 *– The asymmetric unit of complex* ***2.74****. All hydrogen atoms and the non-coordinated water molecules are excluded for clarity.*

Even though the interaction of the ligand with silver in the asymmetric unit is through two of the allyloxy arms, the overall structure shows the ligand acting in a tetradentate manner by using all four allyloxy arms, which leads to a 2D polymeric assembly as shown in Figure 2.63. Interestingly, all the interactions of the ligand occurred through the allyloxy arms unlike complex **2.73**, and also no rearrangement was observed.

Two of the silver atoms (Ag1 and Ag4) are three coordinate, while Ag2 and Ag3 are four coordinate. Each silver atom in the structure is bonding with two olefins; the difference in coordination number of the silver atoms comes from the number of water molecules coordinated.



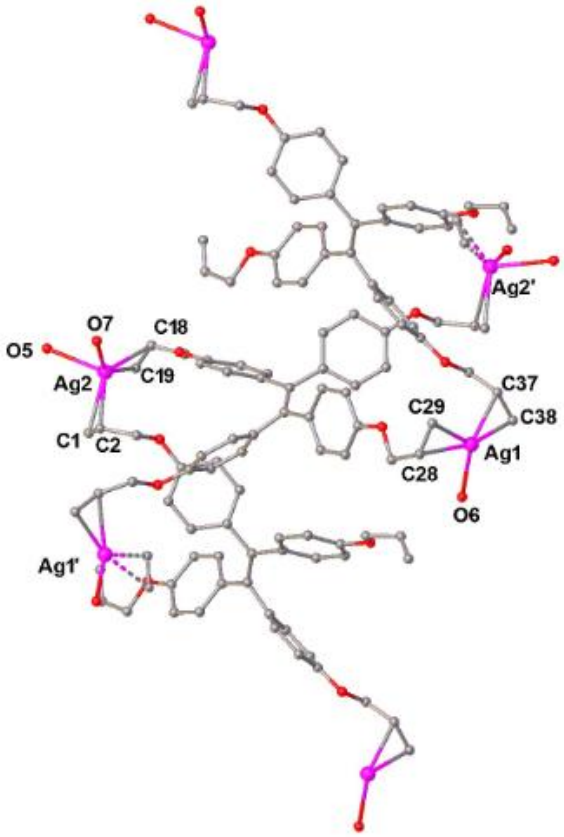


Figure 2.63 *– Part of the 2D polymeric structure of both symmetrically independent assemblies of complex* ***2.74****. All hydrogen atoms, the tetrafluoroborate anions and the non-coordinated water molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O6 2.321(2), Ag1-C28 2.415(3), Ag1-C29 2.384(3), Ag1-C28,C29 2.305(3), Ag1-C37 2.406(3), Ag1-C38 2.334(3), Ag1-C37,C38 2.272(3), O6-Ag1-C28,C29 105.5(1), O6-Ag1-C37,C38 114.5(1), C28,C29-Ag1-C37,C38 134.8(1), Ag2-O5 2.594(2), Ag2-O7 2.310(3), Ag2-C1 2.436(3), Ag2-C2 2.490(3), Ag2-C1,C2 2.370(3), Ag2-C18 2.434(3), Ag2-C19 2.418(3), Ag2-C18,C19 2.332(3), O5-Ag2-O7 90.7(2), O5-Ag2-C1,C2 105.9(1), O5-Ag2-C18,C19 101.3(2), O7-Ag2-C1,C2 105.4(1), O7-Ag2-C18,C19 125.1(1), C1,C2-Ag2-C18,C19 121.5(1), Ag3-C67 2.485(4), Ag3-C68 2.418(3), Ag3-C67,C68 2.369(4), Ag3-O12 2.378(3), Ag3-O13 2.407(2), Ag3-C76 2.425(3), Ag3-C77 2.358(3), Ag3-C76,C77 2.296(3), O12-Ag3-O13 89.7(1), O12-Ag3-C67,C68 86.6(1), O12-Ag3-C76,C77 115.6(1), O13-Ag3-C67,C68 107.7(1), O13-Ag3-C76,C77 104.7(1), C67,C68-Ag3-*

C76,C77 140.6(1), Ag4-C57 2.416(3), Ag4-C58 2.358(3), Ag4-C57,C58 2.290(3), Ag4-O14 2.312(2), Ag4-C40 2.390(3), Ag4-C41 2.432(3), Ag4-C40,C41 2.315(3), O14-Ag4-C57,C58 113.0(1), O14-Ag4-C40,C41 113.8(1), C40,C41-Ag4-C57,C58 127.5(1).

The largest bond angles measured around the environments of Ag1 and Ag4 are between the centroids of the olefins with bond angles of 134.7° and 127.5° respectively. From the measured bond angles around Ag1 and Ag4, both silver atoms have distorted trigonal geometry.

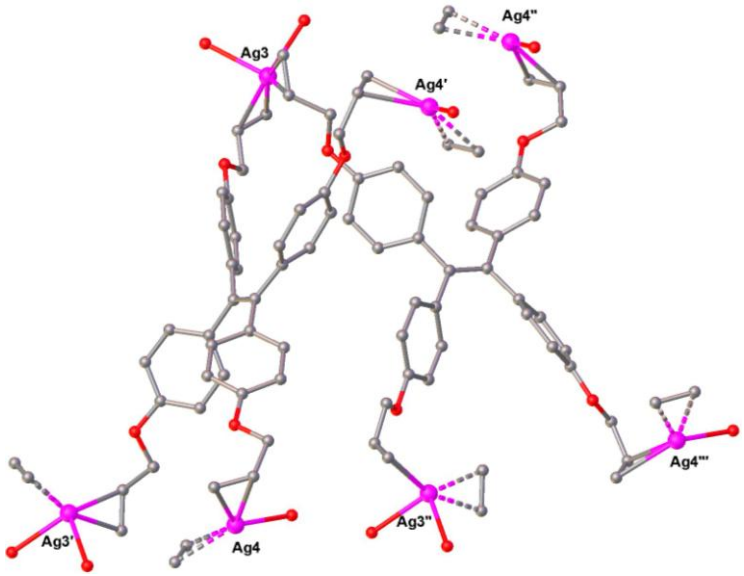
The largest bond angle around the environment of Ag2 is measured between one of the oxygen atoms (O7) and the centroid of the olefin (C18=C19) with a bond angle of 125.1°. The second largest angle is measured between the centroids of the olefins (C1=C2 and C18=C19) with a bond angle of 121.5°. The calculated τ_4 value for Ag2 using these bond angles is 0.80, revealing a trigonal pyramidal shape.

Ag3 is the other four coordinate silver atom with the largest bond angle around its environment measured between the centroids of the olefins (C67=C68 and C76=C77) with a bond angle of 140.6° and the second largest angle is measured between one of the oxygen atoms (O12) and the centroid of C76=C77 with a bond angle of 115.6°. From these bond angles the calculated τ_4 value for Ag2 is 0.74, revealing a seesaw geometry.

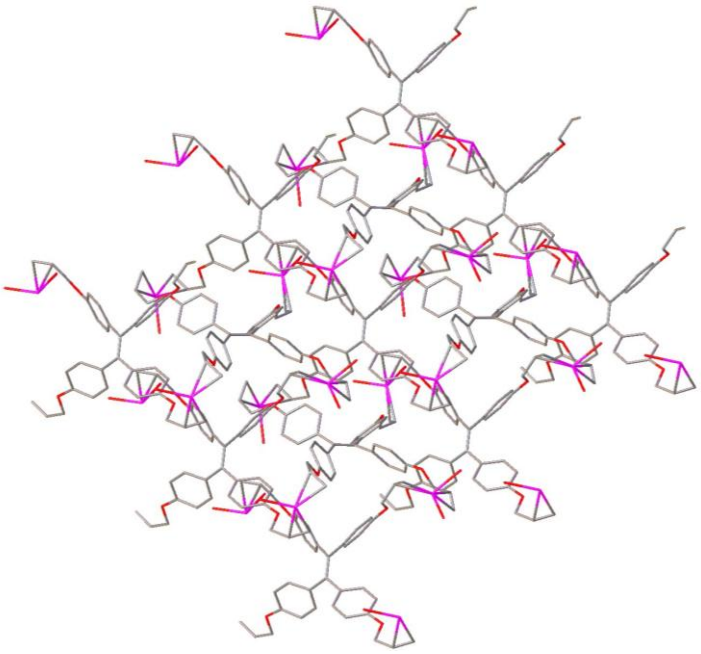
Even though each silver atom in complex **2.74** interacts with two olefins and each ligand has four coordination sites, each silver atom is bridged to six other silver atoms. As shown in Figure 2.64A, Ag3 is bridged to three silver atoms (Ag4, Ag3’ and Ag4’) through the same ligand molecule and to three additional silver atoms (Ag3”, Ag4” and Ag4”’) through the second ligand molecule. The separation distances between the silver atoms range from 8.320 Å to 18.383 Å.

Both ligand **2.54** and **2.62** have four allyloxy arms but the separation distance between the allyloxy groups and the core aromatic groups are different. These differences in the structures of the two ligands lead to significant differences in

the structures of their corresponding complexes. Complex **2.69** and **2.70** are both discrete assemblies; however, the structures of complexes of ligand **2.62** are polymeric assemblies, as shown in complexes **2.72**-**2.74**.



A)



B)

Figure 2.64 *– A) Part of complex* ***2.74*** *showing the ligand bridging Ag3 with six other silver atoms. B) Part of the 2D polymeric structure of complex* ***2.74****.*

*2.5.6 Complex of 1,4-bis(bis(4-allyloxyphenyl)methylidene)cyclohexane (**2.65**)*

With silver(I) triflate (**2.75**)

Crystals of complex **2.75** were grown from the reaction of ligand **2.65** with four equivalents of silver(I) triflate in acetone. The structure of the complex solved in the monoclinic C2/c space group. The asymmetric unit contains half a ligand molecule, one silver atom, one water molecule and a non-coordinated triflate anion, revealing a 1:2 (ligand:metal) ratio complex, as shown in Figure 2.65. Even though the reaction was set up in 1:4 (ligand:silver(I) triflate) ratio, the complex self assembled in a 1:2 (ligand:silver) ratio, as shown in the asymmetric unit of complex **2.75**. One of the allyloxy arms is disordered over two sites with 70% dominant position occupancy.

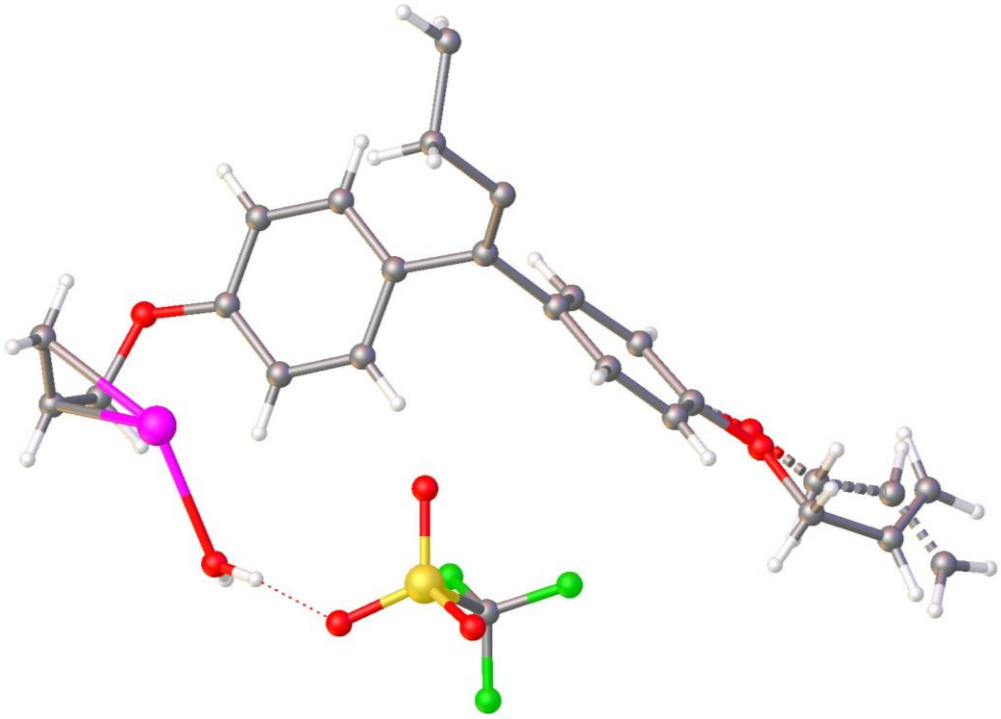


***Figure 2.65** – The asymmetric unit of complex **2.75**. The disordered allyloxy arm is represented with broken bonds.*

The structure of complex **2.75** grows into a 1D-ladder type assembly that involves the interaction of all four allyloxy arms of the ligand with silver, as shown in Figure 2.66A. Interpenetration of two ladder-type structures of

complex **2.75** resulted in a rare 1D-1D polycatenane structure, as shown in Figure 2.66B.

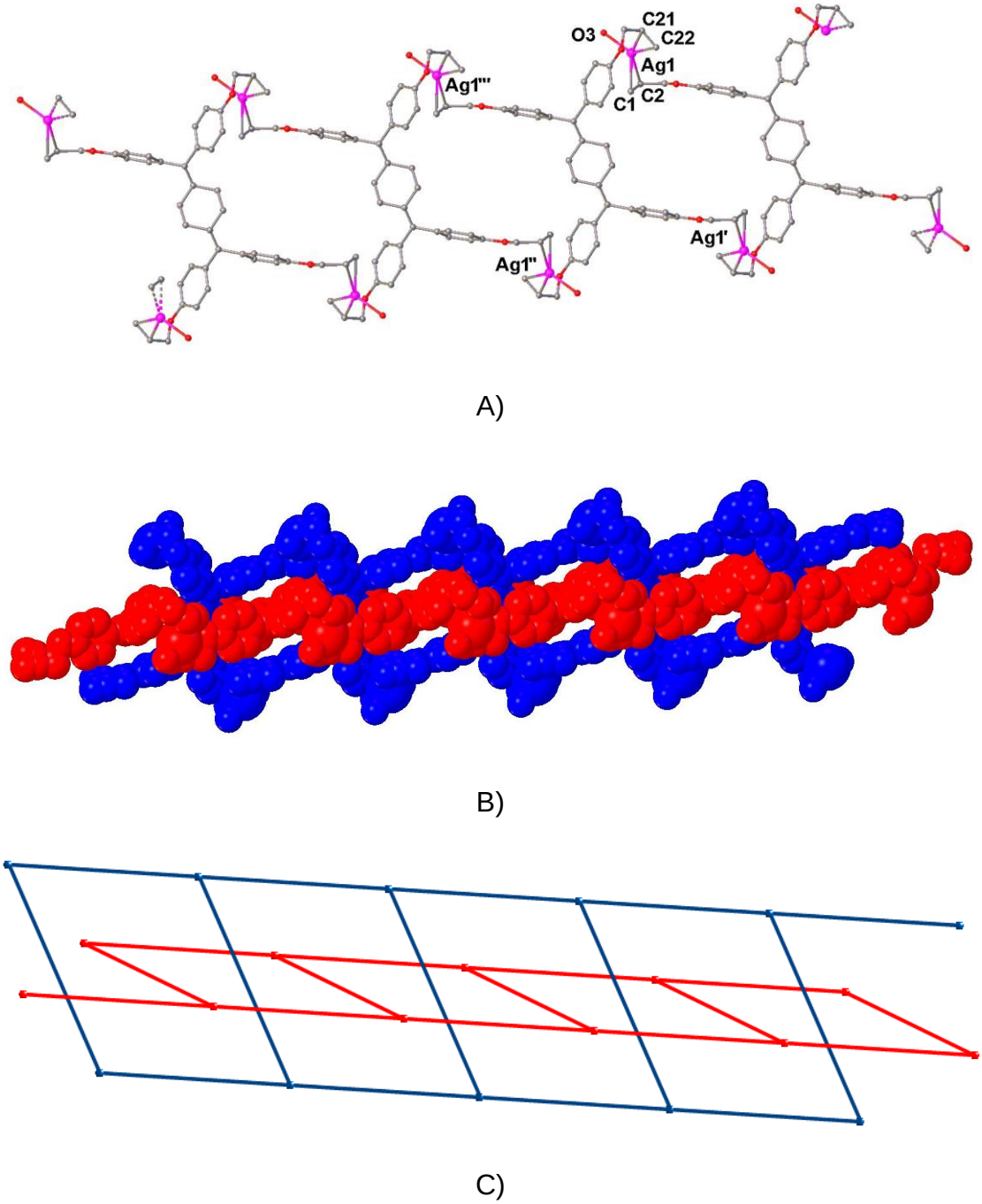


Figure 2.66 *– A) Part of the 1D ladder-type structure that constituents the 1D-1D polycatenane structure of* ***2.75****. B) Part of the 1D-1D polycatenane structure of complex* ***2.75****. C) The simple representation of the 1D-1D polycatenane. All hydrogen atoms, the triflate anions and the disorder are excluded for*

clarity. Selected bond lengths (Å) and angles (°): Ag1-C1 2.380(3), Ag1-C2 2.479(3), Ag1-C1,C2 2.337(3), Ag1-C21 2.432(2), Ag1-C22 2.364(2), Ag1-C21,C22 2.303(2), Ag1-O3 2.292(1), O3-Ag1-C1,C2 113.8(2), O3-Ag1-C21,C22 118.2(2), C1,C2-Ag1-C21,C22 127.6(2).

The silver is three coordinate and is bound to two olefins and one oxygen atom. The three bond angles around Ag1 environment are 127.6°, 118.2° and 113.8°, revealing a trigonal planar geometry.

The ligand bridges four symmetrically related silver atoms with separation distances of (Ag1····Ag1' 13.917 Å, Ag1···Ag1" 14.606 Å and Ag1···Ag1"' 12.129 Å). The ligand bridges silver atoms within the same plane by extending the allyoxy arms in opposite directions. This makes the silver atoms linear connectors that form the sides of the ladder, while the core of the ligand that contain the cyclohexane group acts as the rung of the ladder. As shown in Figure 2.65A, there is a large cavity in the ladder structure that can accommodate the intercalation of another ladder, which results in the polycatenated structure.

Ligand **2.65** acts as a tetradentate ligand by binding all the allyloxy arms. The introduction of the cyclohexane at the core of **2.65** played two significant roles. The first one is increasing the separation distance between the allyloxy arms relative to ligands **2.62** and **2.54**. The second one is introducing flexibility in the ligand especially relative to ligand **2.62**, which has an olefin group between the aromatic rings. The combination of long separation distances between the allyloxy arms and the flexibility of the ligand makes ligand **2.65** a good candidate for the 1D-1D polycatenated structure, shown in Figure 2.66. Batten[167] stated, in his review, that 1D-1D interpenetrated structures would be achievable by the catenation of two ribbons of rings or ladders. Most of the 1D-1D polycatenated structures reported in the literature are due to hydrogen bonding, but recently some work have been reported with metal-ligand interactions.[168]

*2.5.7 Complex of hexakis(allyloxymethyl)benzene (**2.68**)*

With silver(I) perchlorate (**2.76**)

Crystals of complex **2.76** were grown from the reaction of ligand **2.68** with three equivalents of silver(I) perchlorate solution in acetone. The structure of the complex was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains half a ligand molecule, one silver atom and a perchlorate anion, revealing a 1:2 (ligand:metal) ratio complex or an M_2L_1 coordination complex, as shown in Figure 2.67. One of the allyloxy arms of the ligand is disordered over two sites with 82% dominant position occupancy.

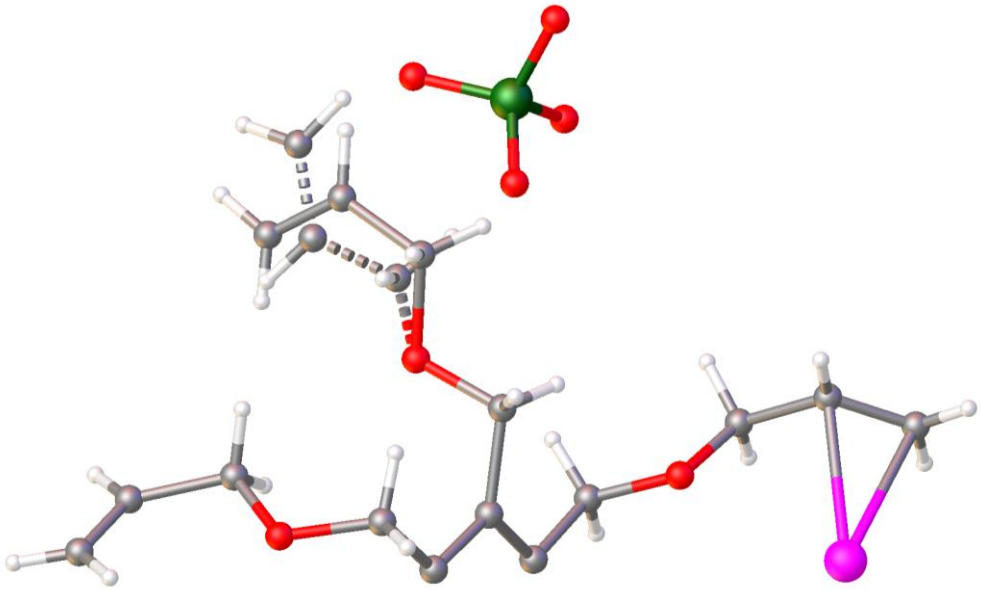


***Figure 2.67** – The asymmetric unit of complex **2.76**, showing half a molecule of ligand **2.68**, a silver atom and a non-coordinated perchlorate anion. The minor component of the disordered allyloxy arm is represented with broken bonds.*

The overall structure of the complex is a 1D polymeric structure that involves the interaction of the six allyloxy arms with four silver atoms. Each silver atom is coordinated with three olefins, two of them are from the same ligand in a chelating manner, while the third is from the second ligand molecule in a bridging manner, as shown in Figure 2.68. Four of the allyloxy arms of the ligand participate in chelating type coordination with two silver atoms, while

the other two allyloxy arms bridge adjacent silver atoms that keep the structure of the complex growing in one dimension. Therefore, the ligand is a hexadentate bridging and chelating type ligand. The interaction of three olefins with a single silver atom without the involvement of additional groups, such as an oxygen atom from the counter anion, is very rare throughout this project.

The interesting feature of the complex is the way the allyloxy arms are positioned relative to the plane of the aromatic ring. Three of the allyloxy arms of the ligand are interacting with silver atoms above the plane of the aromatic ring, while the other three have interactions below the plane of the aromatic ring in an AAABBB type of coordination. This type of interaction is rare in hexadentate ligands with benzene core structures for steric reasons; instead they usually have an ABABAB type of arrangement.[113, 119]The reason why complex **2.76** prefers an AAABBB type of coordination with those long allyloxy groups around the benzene ring over the ABABAB type of interaction is unknown.

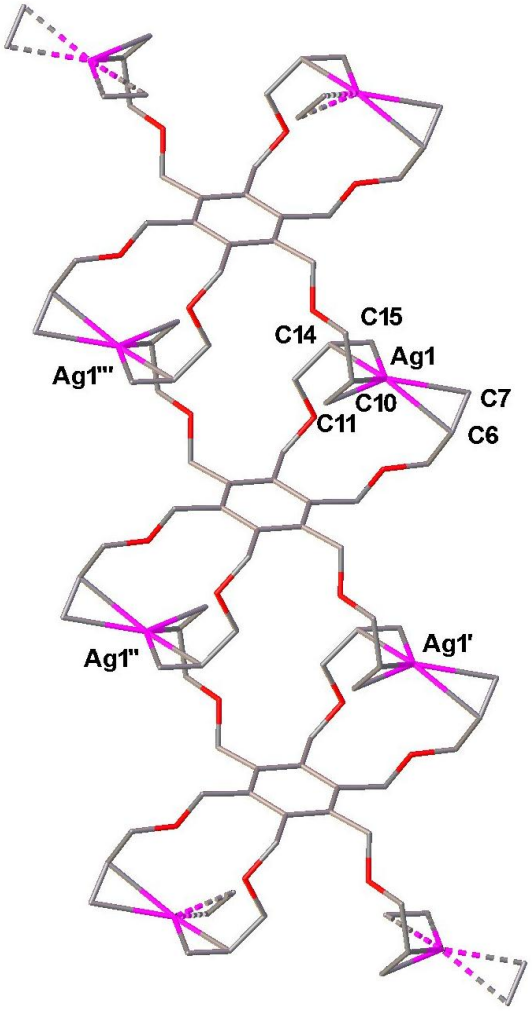


Figure 2.68 *– Part of the 1D polymeric structure of complex* ***2.76****. All hydrogen atoms, the disorder in the allyloxy arm and the perchlorate anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C6 2.539(2), Ag1-C7 2.565(3), Ag1-C6,C7 2.464(3), Ag1-C10 2.540(4), Ag1-C11 2.415(4), Ag1-C10,C11 2.390(4), Ag1-C14 2.498(2), Ag1-C15 2.406(2), Ag1-C14,C15 2.359(2), C6,C7-Ag1-C10,C11 126.4(2), C6,C7-Ag1-C14,C15 114.6(1), C10,C11-Ag1-C14,C15 117.3(2).*

All the silver to individual carbon distances, as well as from the centroid of the olefin to silver, are in the expected silver-carbon bond length range. The three bond angles measured around the environment of Ag1 from the centroids of the olefins are 126.4°, 117.3° and 114.5°, which are close to the ideal trigonal planar geometry (120°).

As shown in Figure 2.68, the ligand bridges four silver atoms using its six allyloxy arms with separation distances 8.520 Å (Ag1···Ag1'), 10.296 Å (Ag1···Ag1"), 7.934 Å (Ag1···Ag1"') and 12.848 Å (Ag1'····Ag1"').

2.6 Summary

This chapter covers the syntheses of eighteen ligands and twenty three complexes. From the eighteen ligands synthesised, eight are new compounds. The ligands range from only one allyloxy arm to six allyloxy arms with different core structures.

Ligands **2.10**, **2.12** and **2.14** represent ligands containing one allyloxy arm. Five complexes of these ligands with different silver(I) salts were obtained and their X-ray structures have been analysed. The complexes of these ligands with different silver(I) salts are discrete assemblies except for **2.10**, which with silver(I) perchlorate gave a 1D polymeric assembly.

Six ligands (**2.20**, **2.21**, **2.26**, **2.27**, **2.31** and **2.32**) were synthesised to investigate the capability of ligands containing two allyloxy arms as new synthons for metallosupramolecular chemistry with different silver(I) salts. All the ligand molecules under this category are built around a bisphenol moiety. Crystals of complexes of these ligands, except for **2.20**, were obtained and analysed using single crystal structure analysis. Ligands **2.21**, **2.26** and **2.27** gave 2D polymeric assemblies, while **2.31** and **2.32** resulted in 1D polymers. In the 2D polymeric assemblies, additional interactions from the carbonyl oxygen (**2.21**) or η^2-type interaction from the aromatic rings of the ligand were involved. In the 1D polymeric assemblies, only the olefin groups of the ligand interact with silver.

Three ligands (**2.45**, **2.46** and **2.48**) were synthesised to investigate the silver-alkene interaction with ligands containing three allyloxy arms. Ligands **2.45** and **2.46** are based on a benzene core structure, while **2.48** is based on a triazine ring. Complexes of both **2.45** and **2.48** gave 2D polymeric structures but attempts to grow crystals of complexes of ligand **2.46** with different silver(I) salts were not successful. The involvement of two of the nitrogen atoms from the triazine core structure in addition to the olefins of the ligand in

the complex structure of **2.48** with silver(I) perchlorate showed the influence of the core structures of ligands in the assemblies of complexes.

Six ligands (**2.53**, **2.54**, **2.59**, **2.62**, **2.65** and **2.68**) were synthesised to investigate the interactions of silver with multi-allyloxy armed ligands. Crystals of silver(I) complexes with these ligands, except for **2.53**, were obtained. Ligand **2.54** gave discrete assemblies with silver(I) perchlorate and silver(I) triflate. Ligand **2.59** also gave a discrete assembly with silver(I) perchlorate.

Ligand **2.62** gave a variety of results ranging from an unexpected rearrangement and cyclization product to 1D-3D polymeric assemblies depending on the type of silver(I) salt used. With silver(I) perchlorate solution in acetone a rearranged product was obtained, while in the presence of acetonitrile a 1D polymeric assembly was obtained. With silver(I) triflate a 3D polymeric assembly was obtained; however, the refinement of the structure is very poor. With silver(I) tetrafluoroborate a 2D polymeric assembly was obtained.

Ligand **2.65** gave a rare 1D-1D polycatenane structure with silver(I) triflate through the coordination of the olefin groups of the ligand. The presence of the cyclohexane ring in the core structure of the ligand is a major factor in the 1D-1D polycatenane assembly by giving the flexibility and the length required for such type of assemblies.

Ligand **2.68** gave a 1D polymeric structure with silver(I) perchlorate. Interestingly, all the allyloxy arms interacted with four silver atoms in an AAABBB fashion. Each silver atom is three coordinate and all of them are bound to the olefins of the allyloxy arms.

Chapter Three

Complexes of ligands containing diallylamine groups

Chapter Three

Complexes of ligands containing diallylamine groups

3.1 Introduction

The use of pyridine rings for the construction of different metallosupramolecular assemblies is useful for various reasons. The main reasons are the rigidity of the aromatic ring and the strong heterocyclic nitrogen interaction with various transition metals. Incorporating these two properties, with the coordination capability of different transition metal atoms has enabled researchers to make complexes with different topologies in a controlled manner. Moreover, multifunctionalisation can be achieved by introducing other groups like arene cores, other heterocyclic rings and single atoms into the core structure of the ligand. The interaction of multifunctionalised ligands can be bridging or chelating depending on the flexibility or rigidity of the ligand, as well as the lability of the transition metal. To induce chelating interactions, different research groups have used ligands that contain di-2-pyridylamine-based heterocycles with a central arene core structure;[169-171] however, some of these ligands act in a bridging manner.[172-175] Keeping the nitrogen atoms of the heterocyclic ring in close proximity to the transition metal, by using the amine moiety, can form chelating type coordination in preference to the bridging mode, as shown in Figure 3.1.

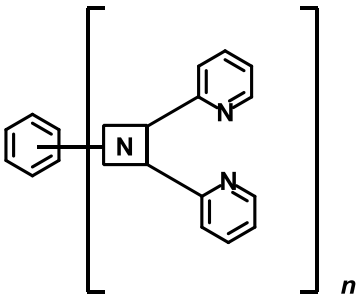


Figure 3.1 *– A schematic diagram of bis(2-pyridyl)amine-based ligands used for chelating type coordination.*

Ligands that conform to this representation have been reported by different research groups, not only for their metallosupramolecular coordination

assembly, but also for other physicochemical functions like luminescence.[176-177] The coordination chemistry of di-2-pyridylamine-based ligands with d^{10} metal ions such as Cu(I), Ag(I) and Zn(II), as a metallosupramolecular assembly, is not rich relative to Cu(II) and other octahedral metal centres. However, there are some examples with Cu(I) as in the work of Barron,[178] who showed by using bis(2-pyridyl)amine (**3.1**) the coordination of the nitrogen atoms of the heterocyclic rings with copper in a chelating mode. Barron also used this system to investigate remote steric control over olefin binding using different aryl substituted bis(2-pyridyl)amines such as **3.2**.[179] Again copper is coordinated through the nitrogen atoms of the pyridyl rings in a chelating mode and is also coordinated with an olefin group from a different ligand. The coordination of different ligands containing bis(2-pyridyl)amine with silver has been reported by the Steel group.[173] In their investigation ligand molecules **3.3**-**3.5**, were used. The positions of the bis(2-pyridyl)amine groups, as well as the spacer core group were changed from benzene to a naphthalene ring.

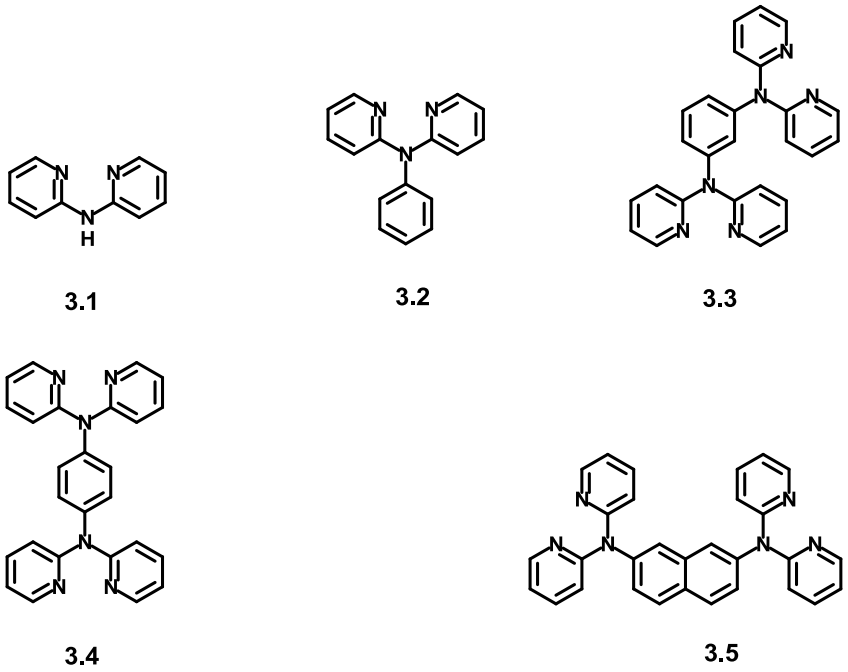
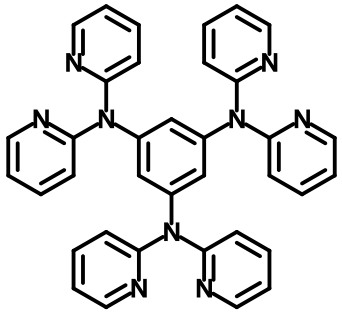
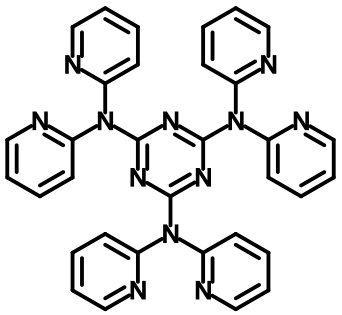


Figure 3.2 *– Bis(2-pyridyl)amine containing ligand molecules previously used for the construction of metallosupramolecular assemblies using Cu(I) or Ag(I) salts.*

One of the interesting features of the use of ligands containing bis(2-pyridyl)amine is the ability to introduce multifunctionalisation into the ligand. Wang *et al.* used ligand molecules **3.6** and **3.7** with different Cu(I) and Ag(I) salts to investigate the impact of the central core arene on the structure, solution dynamics and fluorescence of the complexes.[170] A Cu(I) complex with **3.6** showed the coordination of two of the potential six pyridyl units with copper. The coordinated pyridyl units are from two different dipyridyl amino units and the coordination mode is an 'atypical' chelating mode. The complex of Cu(I) with **3.7** showed the coordination of two bis(2-pyridyl)amine units in a chelating mode, with both pyridyl units from the same dipyridyl amino unit. Interestingly, no coordination of the nitrogen atoms from the triazine ring was observed. Ligand **3.6** complexed with silver nitrate to form a 2D-polymeric assembly, in which all the pyridyl units coordinated with silver. Four of the pyridyl units of **3.6** coordinated with silver in an 'atypical' chelating mode, while the other two coordinated in a terminal binding mode.



3.6



3.7

Figure 3.3 *– Ligands used to investigate the impact of the central core structure of the ligand on the assembly of the complexes by Wang et al.*[170]

The scope of the literature is not limited to ligands containing bis(2-pyridyl)amine. There are a few examples of diallylamine containing ligands used as a metallosupramolecular synthon, one of which is diallylamine (**3.8**). Four binding modes of **3.8** have been reported in the literature involving the coordination of either only the olefin groups, or the combination of the amine nitrogen and the olefin group. All of these complexes are with copper as

shown in Figure 3.4. Ligand **3.8** gave a range of structures varying from discrete ML_2 and M_6L_2 complexes to 1D helical assemblies and 2D metallopolymers with different Cu(I) salts.[60, 180-185] Ligand **3.8** also gave a helical 1D coordination polymer with silver perchlorate.[186]

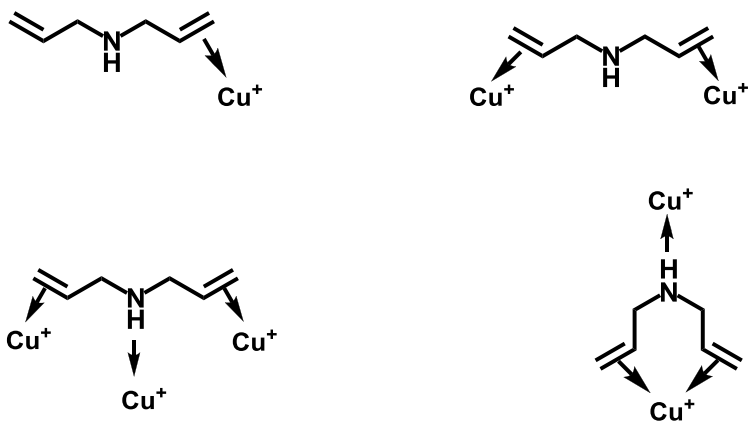


Figure 3.4 *– The four binding modes of* ***3.8*** *with Cu(I).*[60, 180-185]

Having multiple functional groups within a ligand increases the number of potential coordinating sites. In ligand **3.9** multifunctionalisation was achieved, due to the presence of the amine, the diallylamine group and the triazine core. Ligand **3.9** with Ag_2O showed three different modes of coordination involving only the nitrogen atom of the triazine ring or the combinations of the olefin, nitrogen atoms of the triazine ring and the nitrogen atom of the amine, as shown in Figure 3.5. [187]

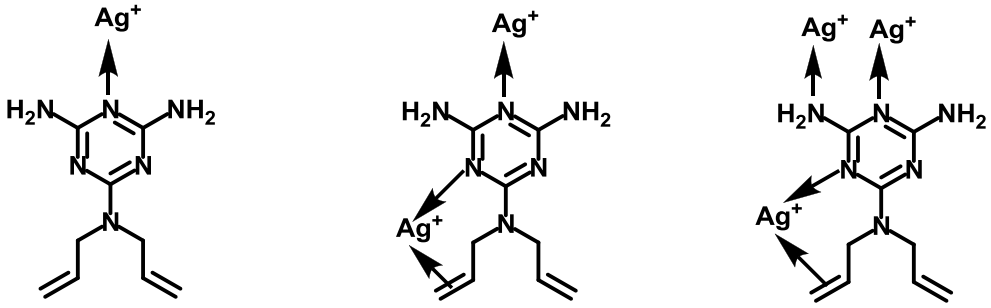
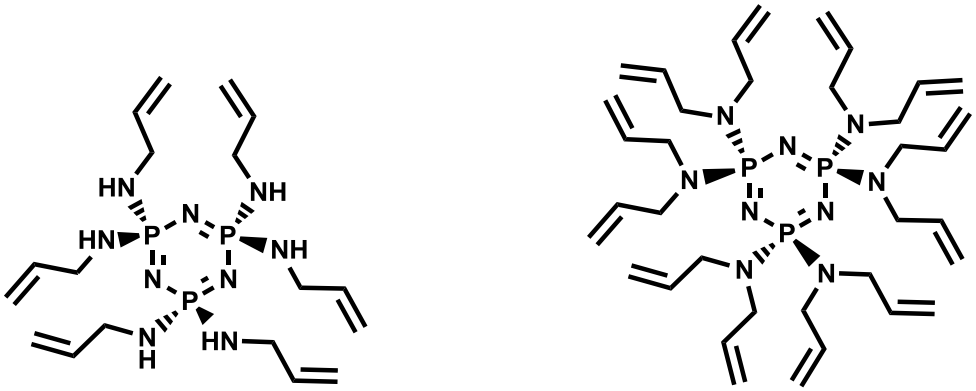


Figure 3.5 *– The three binding modes of* ***3.9*** *with Ag(I).*[187]

One of the advantages of using heterocyclic aromatic cores is the capability of designing multi-allyl armed ligands like **3.10** and **3.11**.[188] Ligand **3.10** formed

a 1D coordination polymer with $AgClO_4$ by coordinating through all six of the allyl arms as well as the triazine nitrogen atoms. Interestingly, this 1D polymer was isomerised into a 3D polymeric assembly. This design concept was further extended into a 12 armed ligand **3.11**, in which all the allyl arms and the nitrogen atoms of the triazine ring coordinated with five silver atoms in a complex that the authors described as “a silver sponge”.[188]



3.10 **3.11**

Figure 3.6 *– Multifunctional ligands used in the literature*.[188]

Compared to the rich chemistry of ligands containing bis(2-pyridyl)amine group in metallosupramolecular chemistry, the ligands containing diallylamine group have been much less studied. This chapter will cover the work done on ligands containing diallylamine group as new metallosupramolecular synthons for silver-alkene interactions. The ligands are divided into three subclasses depending on their number of diallylamine groups.

3.2 Ligands containing one diallylamine group.

The coordination of ligands containing one diallylamine group with silver has been studied by using compounds shown in Figure 3.7.

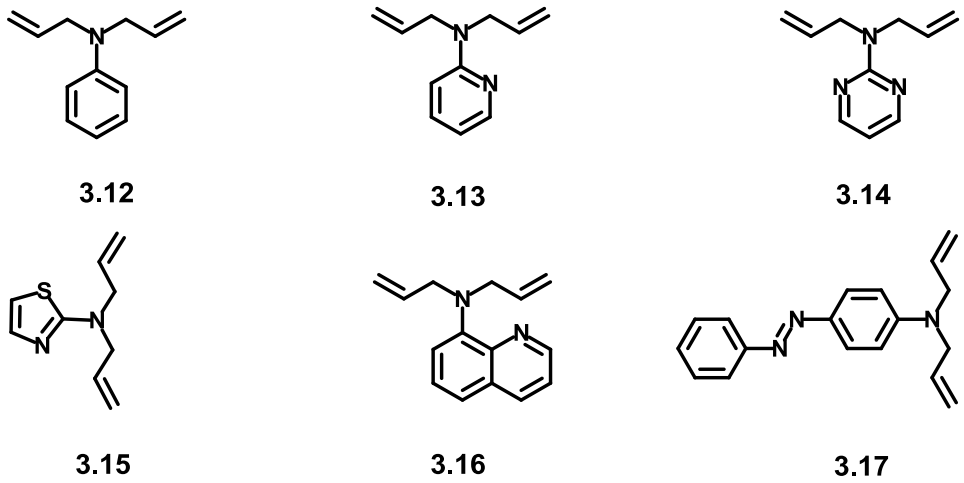
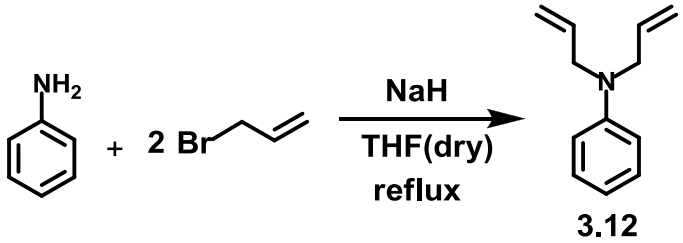


Figure 3.7 *– Ligands containing one diallylamine group.*

3.2.1 Synthesis of ligands containing one diallylamine group

Ligands **3.12**-**3.17** were synthesised from their corresponding amine groups by using a common procedure, as shown in scheme 3.1.



Scheme 3.1 – Synthesis of **3.12** from aniline.

Ligand **3.12** was synthesised from aniline using a literature method,[151] as shown in scheme 3.1. In the literature, the purification using vacuum distillation resulted in a 30% yield; however, in our synthesis it was purified using silica gel column chromatography in 30:70 (ethyl acetate:petroleum ether) solvent ratio in 97% yield. Ligands **3.13**–**3.17** were synthesised from their corresponding aryl amines using the above method in 46-92% yields.

*3.2.2 Complex of N,N-diallylaminobenzene (**3.12**)*

With silver(I) perchlorate (**3.18**)

Ligand **3.12** was mixed with two equivalents of silver(I) perchlorate in acetone. Diethyl ether was allowed to diffuse into the reaction mixture, which resulted in

the growth of crystals suitable for X-ray crystal structure analysis. The structure was solved in the orthorhombic space group $P2_12_12_1$. The asymmetric unit contains one full ligand molecule, one silver atom and a non-coordinated perchlorate counter anion, revealing a 1:1 (metal:ligand) ratio or an M_1L_1 type complex, as shown in Figure 3.8.

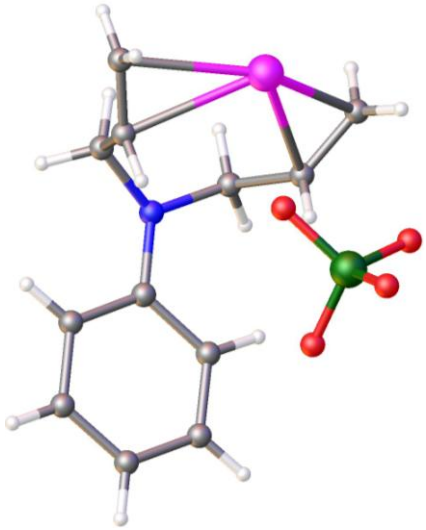


Figure 3.8 *– The asymmetric unit of complex* ***3.18*** *showing the coordination of both allyl arms with silver, while the perchlorate anion is non-coordinated.*

The structure grows into a 1D zigzag polymeric assembly through the coordination of the two allyl arms in a chelating mode and the *para* carbon atom of the benzene ring in a η^1-mode, as shown in Figure 3.9. The η^2-type coordination of silver with the olefin functional group and η^1-mode with the aromatic ring has been reported previously by Whitcomb *et al.*[189] in the discrete silver(I) complex of 4-phenylbut-1-ene. The η^1-type coordination of the aromatic rings with silver has been well studied by Munakata *et al.*[80] The bond distance observed in the η^1 coordination mode in complex **3.18** is 2.454 Å, which is shorter than the separation distance (2.547(6) Å and 2.692(5) Å) reported in the literature.[189] The interesting feature of complex **3.18** is the chelating coordination mode of the two allyl arms with silver. This is the only example of chelation of allyl arms from the same diallylamine group with a benzene ring core structure. The chelation of the allyl arms originated from the same nitrogen atom observed in triallylamine complexes with various silver(I)

salts.[60] This has also been observed in the complex of 1,8-di(allyloxy)naphthalene with silver(I) triflate, also involving the coordination of the two allyl ether arms with silver in a chelating manner accompanied by η^2-coordination of the naphthalene ring with silver to generate a [2+2] macrocycle.[60]

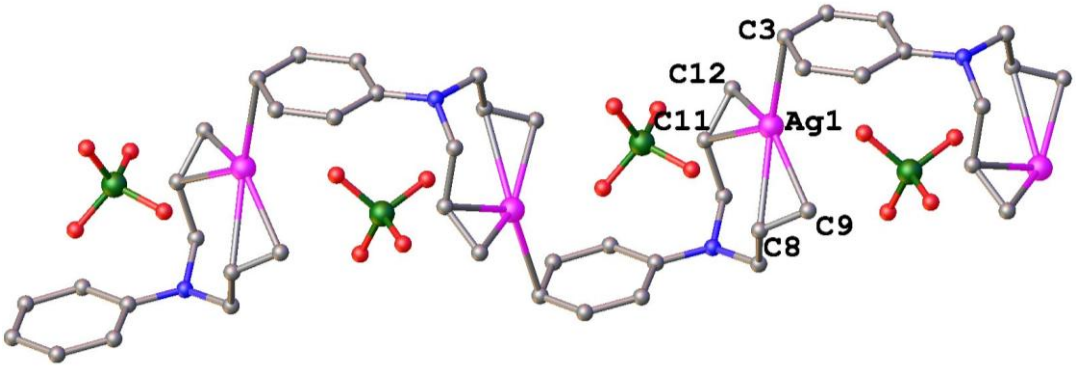


Figure 3.9 *– Part of the 1D zigzag polymeric structure of complex* ***3.18****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C8 2.466(2), Ag1-C9 2.386(2), Ag1-C8,C9 2.331(2), Ag1-C11 2.471(2), Ag1-C12 2.424(2), Ag1-C11,C12 2.354(2), Ag1-C3 2.454(2), C8-Ag1-C11 87.9(2), C8-Ag1-C12 118.5(2), C9-Ag1-C11 118.0(2), C9-Ag1-C12 144.3(2), C8,C9-Ag1-C11,C12 117.4(2), C8-Ag1-C3 136.4(2), C9-Ag1-C3 113.1(2), C8,C9-Ag1-C3 125.7(2), C11-Ag1-C3 127.1(2), C12-Ag1-C3 102.0(2), C11,C12-Ag1-C3 115.1(2).*

The coordination of the allyl arms with silver is in a “cis-manner” where both allyl arms face in the same direction. Another interesting feature of the structure is that both the allyl arms and the phenyl ring are coordinated from the same face, either from the top or bottom of the plane of the complex. The η^1-coordination mode of the carbon atom of the phenyl ring is *para* to the carbon atom attached to the amine nitrogen. It seems the amine group is donating electron density towards the aromatic ring resulting in a higher electron density at the *para* position which enables coordination with silver. The perchlorate anions are non-coordinated; the closest distance between an

oxygen atom of the anion and the silver is 2.691 Å, which is too far to represent any considerable interaction. The perchlorate anions sit within the troughs of the zigzag assembly, as shown in Figure 3.9. All the silver-carbon bond distances are in the expected range for silver olefinic or aromatic carbon interactions. The Ag1-C3 bond distance (2.454 Å) is longer than the bond distances between the centroids of the coordinated olefinic carbons and silver (C8,C9-Ag1 2.331 Å and C11,C12-Ag1 2.354 Å). The silver is three coordinate with bond angles 125.7°, 115.1° and 117.4° with the centroids of the coordinated olefin carbon atoms and the aromatic carbon. From the measured bond angles silver has a trigonal planar geometry. In general, the ligand molecule acts as both a chelating and bridging ligand with the Ag····Ag separation across ligand **3.12** being 6.304 Å.

*3.2.3 Complex of 2-(N,N-diallylamino)pyridine (**3.13**)*

With silver(I) perchlorate (**3.19**)

Ligand **3.13** was mixed with two equivalents of silver(I) perchlorate in acetone. Diethyl ether diffusion into the reaction mixture followed by slow evaporation of the solvent resulted in the growth of colourless blocks suitable for X-ray structure study. The structure was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand molecule, one silver atom and a coordinated perchlorate anion, revealing a 1:1 (metal:ligand) ratio or M_1L_1 type complex, as shown in Figure 3.10.

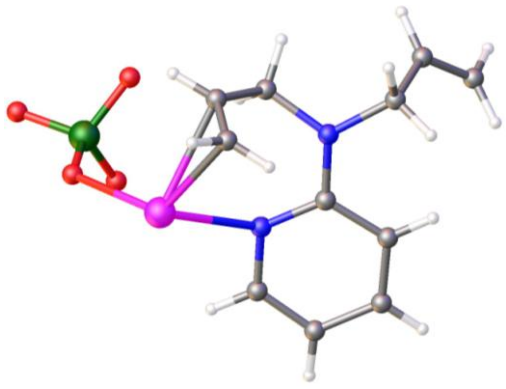
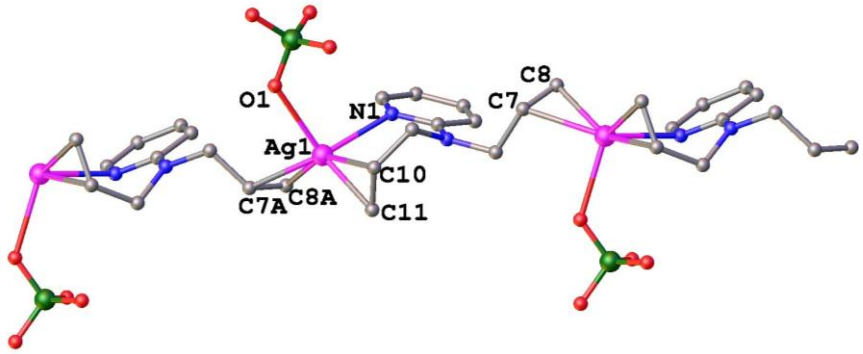
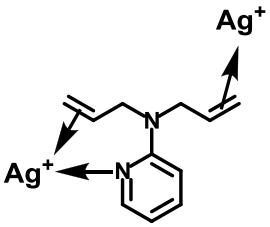


***Figure 3.10** – The asymmetric unit of complex **3.19**.*

The structure grows into a 1D zigzag polymeric assembly involving the coordination of one of the allyl arms and the pyridyl nitrogen with silver in a chelating mode, while the other allyl arm coordinates to a neighbouring silver atom in a bridging mode. The two allyl arms from the same amine group coordinated with silver in a “trans-manner”, as shown in Figure 3.11A. For instance, the position of the allyl arm containing the C7=C8 double bond is above the plane of the complex, while the C10=C11 bond is below the plane of the complex. This mode of coordination can be represented in a simple diagram, as shown in Figure 3.11B.



A)



B)

Figure 3.11 *–A) Part of the 1D polymeric structure of complex* ***3.19****. All hydrogen atoms have been omitted for clarity. B) The binding mode observed in complex* ***3.19****. Selected bond lengths (Å) and angles (°): Ag1-O1 2.454(2), Ag1-N1 2.402(2), Ag1-C10 2.462(2), Ag1-C11 2.447(2), Ag1-C10,C11 2.363(2), Ag1-C7A 2.489(2), Ag1-C8A 2.374(2), Ag1-C7A,C8A 2.338(2), O1-Ag1-N1 99.9(2), O1-Ag1-C10 100.1(2), O1-Ag1-C11 128.3(2), O1-Ag1-C10,C11 114.4(2), O1-Ag1-C7A 89.2(1), O1-Ag1-C8A*

107.9(2), O1-Ag1-C7A,C8A 98.6(1), N1-Ag1-C10 83.3(1), N1-Ag1-C11 92.1(1), N1-Ag1-C10,C11 87.6(1), N1-Ag1-C7A 132.4(1), N1-Ag1-C8A 102.7(1), N1-Ag1-C7A,C8A 118.1(1), C10-Ag1-C7A 141.4(2), C10-Ag1-C8A 149.7(2), C11-Ag1-C7A 118.5(2), C11-Ag1-C8A 118.3(2), C10,C11-Ag1-C7A,C8A 134.5(2).

The silver is four coordinate from two olefin groups of the allyl arms of neighbouring ligand molecules, the pyridyl nitrogen of the ligand and an oxygen of the perchlorate anion. The largest angle is between the centroids of the coordinated olefin groups (134.5°) and the second largest angle is measured between the pyridyl nitrogen (N1) and the centroid of the coordinated olefin group (C7A,C8A) with a bond angle of 118.0°. The calculated τ_4 value for silver is 0.76, indicating a seesaw geometry. The perchlorate counter anions interact with silver alternatively above and below the plane of the chain. All the silver-carbon bond distances are within the expected bond distances for silver-olefin η^2-type interactions. In comparison to complex **3.18**, the pyridyl nitrogen of the heterocyclic ring influences the coordination of the allyl arms from the same amine group. The nitrogen atom of the pyridyl ring (N1) and the closest allyl arm of the diallylamine chelates with silver, while the other allyl arm bridges with the neighbouring silver atom. Due to the introduction of the heterocyclic nitrogen atom in complex **3.19**, the coordination of the aromatic ring through the *para* carbon atom is not observed. Ligand **3.13** bridges silver atoms with a separation distance of 8.219 Å.

*3.2.4 Complexes of 2-(N,N-diallylamino)pyrimidine (**3.14**)*

With silver(I) perchlorate (**3.20**)

Ligand **3.14** was mixed with two equivalents of silver(I) perchlorate in acetone. As soon as the ligand was mixed with the silver(I) perchlorate solution, a white precipitate formed. The white precipitate was dissolved in a mixture of THF, water and acetone. Slow evaporation of the solvent resulted in the growth of tiny crystals suitable for X-ray crystallographic study. The structure was solved

in the orthorhombic $P2_12_12$ space group. The asymmetric unit contains two full ligand molecules, two silver atoms, one non-coordinated perchlorate anion and two half non-coordinated perchlorate anions, revealing a 1:1 (metal:ligand) ratio or M_2L_2 type coordination complex, as shown in Figure 3.12. The diallylamine group of one of the ligand molecules in the asymmetric unit has disorder over two sites with 55% dominant position occupancy. The structure grows into a 1D zigzag polymeric chain involving the coordination of both nitrogen atoms of the pyrimidine ring and the allyl arms of the ligand with two crystallographically independent silver atoms. Similar to complex **3.19,** the allyl arms from the same amine group coordinate to silver in a “trans-mode”. Again the pyrimidine nitrogen atoms influence the way the allyl arms coordinate with silver. As shown in Figure 3.13, one of the allyl arms (C5=C6) and the pyrimidinyl nitrogen atom (N2) are connected with the first silver atom (Ag1), while the other allyl arm (C1=C2) and the pyrimidinyl nitrogen atom (N1) of the ligand are connected with the second silver atom (Ag2). It seems the pyrimidine nitrogen atoms pull the allyl arms of the amine group in opposite directions.

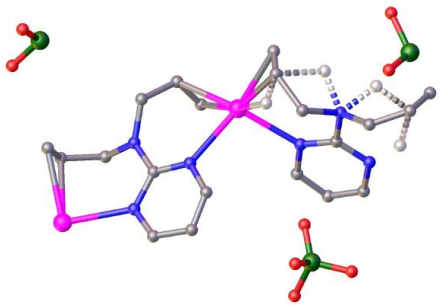


Figure 3.12 *– The asymmetric unit of complex* ***3.20****. All hydrogen atoms have been omitted for clarity.*

The ligand again acts in both a chelating and bridging manner. The ligand bridges the two crystallographically independent silver atoms with an Ag1···Ag2 separation distance of 6.662 Å, which is shorter than the separation distance observed in complex **3.19**. The shorter separation distance in complex **3.20** is the result of chelation of the pyrimidine nitrogen atoms and the allyl arms to silver in both directions of the polymer. Both silver atoms are four coordinate and the coordinated groups are the same.

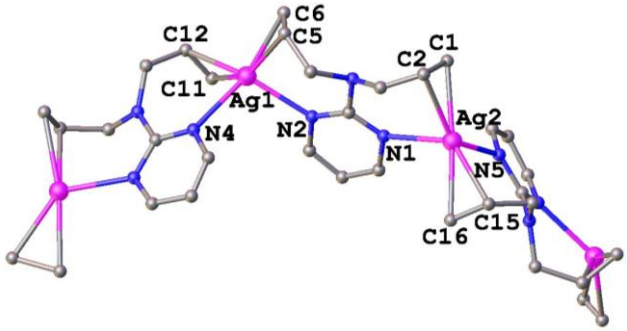


Figure 3.13 *– Part of the 1D polymeric structure of complex* ***3.20****. All hydrogen atoms, the disorder observed in one of the ligand molecules and the perchlorate anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N2 2.344(1), Ag1-N4 2.417(2), Ag1-C11 2.354(1), Ag1-C12 2.466(1), Ag1-C11,C12 2.319(1), Ag1-C5 2.422(2), Ag1-C6 2.375(2), Ag1-C5,C6 2.339(2), N2-Ag1-N4 104.4(4), N2-Ag1-C11 106.0(4), N2-Ag1-C12 137.3(3), N2-Ag1-C11,C12 122.0(4), N2-Ag1-C5 87.1(4), N2-Ag1-C6 93.1(1), N2-Ag1-C5,C6 90.1(3), N4-Ag1-C11 88.3(3), N4-Ag1-C12 84.0(3), N4-Ag1-C11,C12 85.9(3), N4-Ag1-C5 115.6(2), N4-Ag1-C6 137.1(2), N4-Ag1-C5,C6 126.5(2), C11-Ag1-C6 124.4(2), C11-Ag1-C5 149.4(2), C12-Ag1-C5 127.5(4), C12-Ag1-C6 109.1(2), C11,C12-Ag1-C5,C6 128.8(3). Ag2-N5 2.333(2), Ag2-C15 2.486(1), Ag2-C16 2.425(1), Ag2-C15,C16 2.368(1), Ag2-N1 2.424(2), Ag2-C2 2.470(2), Ag2-C1 2.437(2), Ag2-C1,C2 2.328(2), N5-Ag2-C15 86.6(3), N5-Ag2-C16 91.5(3), N5-Ag2-C15,C16 88.9(3), N5-Ag2-N1 98.0(3), N5-Ag2-C2 135.2(3), N5-Ag2-C1 98.8(2), N5-Ag2-C1,C2 117.2(2), C15-Ag2-N1 132.9(2), C15-Ag2-C2 125.0(4), C15-Ag2-C1 144.8(2), C16-Ag2-N1 102.1(2), C16-Ag2-C2 132.4(4), C16-Ag2-C1 168.7(2), C15,C16-Ag2-C1,C2 146.1(2), N1-Ag2-C2 83.1(3), N1-Ag2-C1 81.1(2), N1-Ag2-C1,C2 81.6(3).*

The largest bond angle for Ag1 is between the centroids of the coordinated olefin groups with a bond angle of 128.8° and the second largest bond angle

is between the heterocyclic nitrogen atom (N4) and the centroid of the olefin group (C5=C6) with a bond angle of 126.5°. The calculated τ_4 value for Ag1 is 0.74, indicating a seesaw geometry. The largest bond angle for Ag2 is between the centroids of the two coordinated olefin groups with a bond angle of 146.1° and the second largest bond angle is between one of the coordinated heterocyclic nitrogen atoms(N1) and the centroid of the olefin group (C15=C16) with a bond angle of 117.7°. The calculated τ_4 value for Ag2 is 0.68, again revealing a seesaw geometry.

With silver(I) triflate (**3.21**)

Ligand **3.14** was mixed with two equivalents of silver(I) triflate in acetone and diethyl ether was diffused into the reaction mixture. Tiny crystals were grown within a day, which were suitable for X-ray crystal structure analysis. The structure was solved in the orthorhombic $P2_12_12_1$ space group. The asymmetric unit contains two ligand molecules, two silver atoms, a coordinated water molecule and two non-coordinated triflate counter anions, revealing a 1:1 (metal:ligand) ratio or an M_2L_2 type coordination complex, as shown in Figure 3.14.

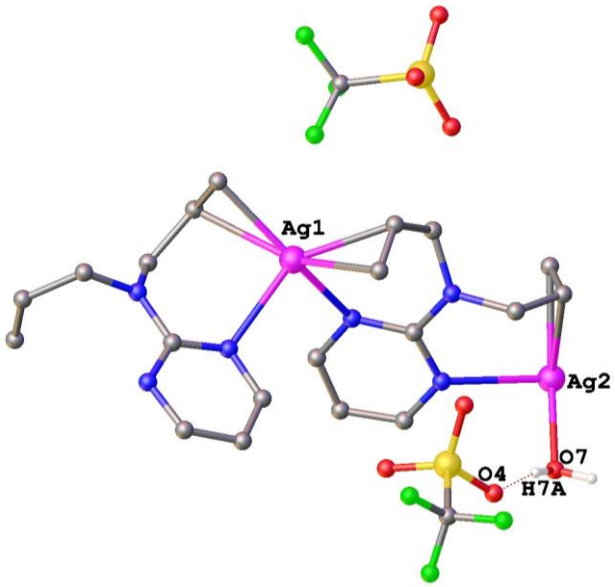


Figure 3.14 *- The asymmetric unit of complex* ***3.21****. All hydrogen atoms except the water molecule are omitted for clarity.*

The full structure grows into a 1D zigzag polymeric assembly through the coordination of the two allyl arms and the pyrimidine nitrogen atoms with silver. Similar to complex **3.20**, the allyl arms of the ligand from the same amine group are coordinated with silver in a “trans-mode”. Again ligand **3.14** doubly bridges the two crystallographically independent silver atoms through the coordination of the allyl arms and the pyrimidine nitrogen with silver, similar to complex **3.20**. Unlike complex **3.20**, the two silver atoms have two different coordination numbers, as shown in Figure 3.15.

Ag1 is four coordinate from the coordination of two allyl arms (C9=C10, C16=C17) and two pyrimidine nitrogen atoms (N2, N4) from adjacent ligands. The largest bond angle is measured between the coordinated heterocyclic nitrogen (N4) and the centroid of the olefin group of the allyl arm from the adjacent ligand (C9=C10) with a bond angle of 137.5°. The second largest angle is between the centroids of the olefinic carbon atoms with a bond angle of 128.4°. The calculated τ_4 value for Ag1 is 0.67, revealing a seesaw geometry.

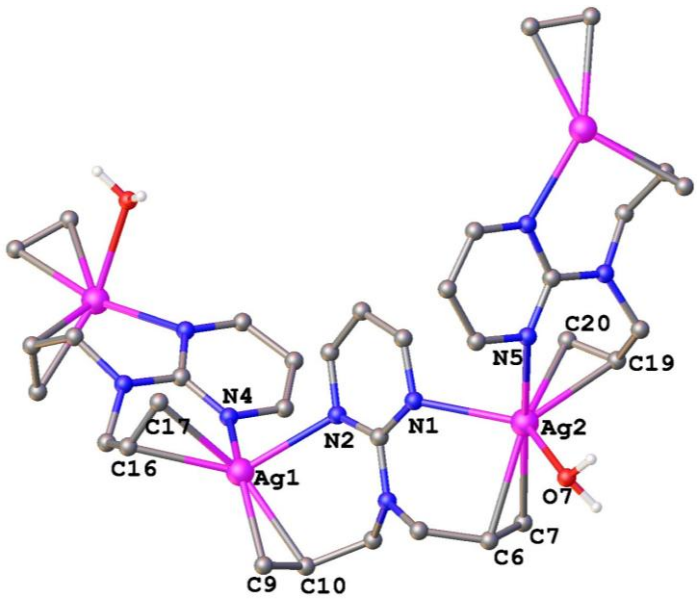


Figure 3.15 *– Part of the 1D zigzag polymeric structure of complex* ***3.21****. All hydrogen atoms (except for the water molecule) and the triflate counter anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C16*

2.444(3), Ag1-C17 2.471(3), Ag1-C16,C17 2.367(3), Ag1-N4 2.379(3), Ag1-C9 2.443(3), Ag1-C10 2.385(3), Ag1-C9,C10 2.321(3), Ag1-N2 2.424(2), C16-Ag1-N4 85.1(2), C17-Ag1-N4 89.5(1), C16,C17-Ag1-N4 87.3(2), C16-Ag1-C9 135.5(1), C16-Ag1-C10 108.2(1), C17-Ag1-C9 146.9(2), C17-Ag1-C10 115.5(1), C16,C17-Ag1-C9,C10 128.5(1), C16-Ag1-N2 132.5(1), C17-Ag1-N2 101.7(1), C16,C17-Ag1-N2 117.0(1), N4-Ag1-C9 123.1(1), N4-Ag1-C10 151.1(1), N4-Ag1-C9,C10 137.5(1), N4-Ag1-N2 91.6(2), C9-Ag1-N2 84.7(2), C10-Ag1-N2 97.2(2), C9,C10-Ag1-N2 90.9(2). Ag2-C19 2.467(3), Ag2-C20 2.462(3), Ag2-C19,C20 2.373(3), Ag2-N5 2.588(2), Ag2-O7 2.399(3), Ag2-C6 2.634(3), Ag2-C7 2.569(3), Ag2-C6,C7 2.516(3), Ag2-N1 2.441(2), C19-Ag2-N5 80.3(1), C20-Ag2-N5 86.0(1), C19,C20-Ag2-N5 82.9(1), C19-Ag2-O7 102.7(1), C20-Ag2-O7 133.7(1), C19,C20-Ag2-O7 118.2(1), C19-Ag2-C6 133.0(1), C19-Ag2-C7 105.9(1), C20-Ag2-C6 132.8(1), C20-Ag2-C7 104.0(1), C19,C20-Ag2-C6,C7 120.4(1), C19-Ag2-N1 125.3(1), C20-Ag2-N1 94.4(1), C19,C20-Ag2-N1 109.9(1), N5-Ag2-O7 76.7(2), N5-Ag2-C6 141.2(2), N5-Ag2-C7 169.1(2), N5-Ag2-C6,C7 84.4(2), N5-Ag2-N1 92.9(2), O7-Ag2-C6 76.4(1), O7-Ag2-C7 92.9(1), O7-Ag2-C6,C7 84.4(1), O7-Ag2-N1 128.6(1), C6-Ag2-N1 82.7(2), C7-Ag2-N1 90.9(2), C6,C7-Ag2-N1 86.7(2).

Ag2 is five coordinate with a calculated τ_5 value of 0.14, which reveals a twisted square pyramidal geometry through the coordination of a water molecule, pyrimidine nitrogen atoms (N1, N5) and the allyl arms (C6=C7, C19=C20) of the ligands. Some of the bond distances measured between Ag2 and the coordinated olefinic carbon atoms and also the nitrogen atom of the pyrimidine ring are longer than the measured bond distances in complexes **3.19** and **3.20**. The Ag2-C6 bond distance (2.634 Å) and the Ag2-C7 (2.569 Å), as well as the measured bond distance between the centroid of the olefin group to silver (Ag2-C6,C7 2.516 Å), are longer than the measured bond distances in the previous complexes. The Ag2-N5 bond distance (2.588 Å) is

also longer than the measured bond distances in complexes **3.19** and **3.20**. The largest bond angle is measured between the centroid of the olefin (C6=C7) and the nitrogen atom (N5) of the pyrimidine ring with a bond angle of 155.4°. The second largest angle is measured between the water molecule (O7) and the nitrogen atom (N1) of the pyrimidine ring from the adjacent ligand with a bond angle of 128.6°. From the measured bond distances and angles, the pyrimidine ring nitrogen atoms have considerable pyrimidalization. There are two different Ag1····Ag2 separation distances (6.697 Å and 6.865 Å), which are shorter than the Ag····Ag separation distance observed in complex **3.19**, but similar to that observed in complex **3.20**. Although the triflate counter anion is not coordinated, it has a hydrogen bonding interaction with the water molecule, as shown in Figure 3.14. The coordinated water molecule acts as a hydrogen bonding donor and the oxygen atom of the triflate anion as a hydrogen bond acceptor. The relevant bond distances and angles are shown in the following table.

D-H····A	D-H	H···A	D···A	D-H···A
O7-H7A···O	0.870	1.865	2.725	169.76

Table 3.1 *Hydrogen bonding geometry between the coordinated water molecule and the triflate counter anion.*

In general, the interaction of ligand **3.14** with silver(I) perchlorate and silver(I) triflate observed in complexes **3.20** and **3.21**, can be represented by the following Figure.

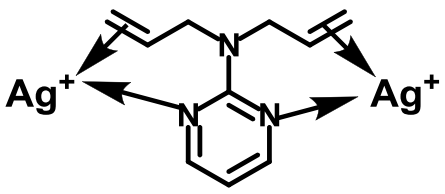


Figure 3.16 *– simple representation of the mode of interaction of ligand **3.14** with silver(I) salts.*

*3.2.5 Complex of 2-(N,N-diallylamino)thiazole (**3.15**)*

With silver(I) triflate (**3.22**)

Ligand **3.15** was mixed with two equivalents of silver(I) triflate in toluene. Diethyl ether diffusion into the reaction mixture resulted in the growth of crystals suitable for X-ray structure analysis over two weeks. The structure was solved in the triclinic P-1 space group. The asymmetric unit contains two full ligand molecules, two silver atoms and two non-coordinated triflate counter anions, revealing a 1:1 (metal:ligand) ratio or an M_1L_1 coordination complex, as shown in Figure 3.17. One of the non-coordinated triflate anions, the diallylamine of one of the ligand molecules, the thiazole sulfur atom and one of the allyl arms of the second ligand molecule are disordered over two sites. The dominant site occupancy of the diallyl arm, the thiazole sulfur and the allyl arm of the other ligand is 63%, while for the triflate counter anion, it is 80%.

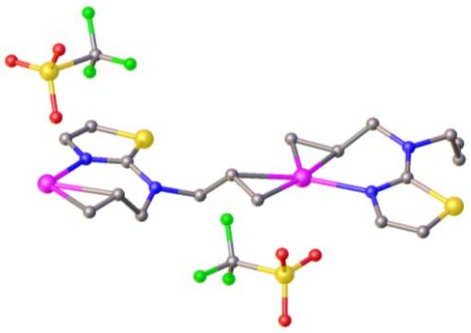


***Figure 3.17** – The asymmetric unit of complex **3.22**. All hydrogen atoms, the disorder observed in the allyl arms, sulphur atom and the triflate counter anion have been omitted for clarity.*

The structure grows into a 1D polymeric assembly through the coordination of both allyl arms and the nitrogen atom of the thiazole ring. The sulfur atom of the thiazole ring is not coordinated. It seems silver preferentially coordinates with the olefin group and the nitrogen atom of the thiazole ring in preference to the sulfur atom. The allyl arm and the nitrogen atom of the thiazole ring chelates with silver as observed in complexes **3.18**-**3.20**. The ligand alternates its position above and below the plane of the polymeric chain which keeps the coordinating sites at the right position for extension of the polymeric chain, as

shown in Figure 3.18. The ligand bridges adjacent silver atoms through the coordination of the allyl arms with an Ag1····Ag2 separation distance of 8.042 Å. This separation is longer than that measured in complexes **3.19** and **3.20**, but shorter than that in complex **3.18**.

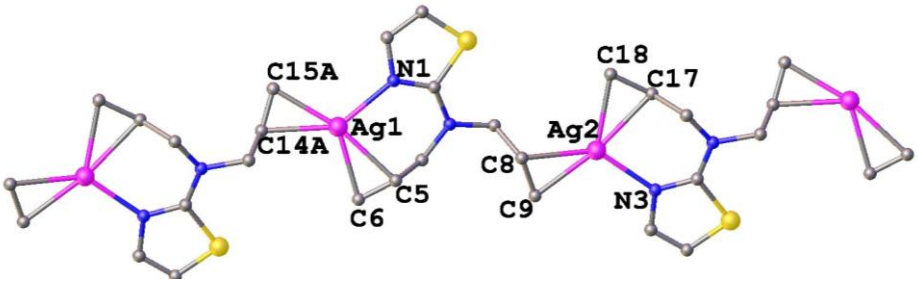


Figure 3.18 *– Part of the polymeric structure of complex* ***3.22****. All hydrogen atoms, the disorder and the triflate counter anions are omitted. Selected bond lengths (Å) and bond angles (°): Ag1-N1 2.205(3), Ag1-C5 2.427(2), Ag1-C6 2.351(2), Ag1-C5,C6 2.300(2), Ag1-C14A 2.338(4), Ag1-C15A 2.299(2), Ag1-C14A,C15A 2.221(3), N1-Ag1-C5 82.9(2), N1-Ag1-C6 113.9(4), N1-Ag1-C5,C6 98.1(3), N1-Ag1-C14A 143.1(2), N1-Ag1-C15A 109.8(2), N1-Ag1-C14A,C15A 126.6(2), C5-Ag1-C14A 134.0(3), C5-Ag1-C15A 167.1(3), C6-Ag1-C14A 102.8(4), C6-Ag1-C15A 135.8(4), C5,C6-Ag1-C14A,C15A 135.1(4), Ag2-C8 2.387(2), Ag2-C9 2.336(2), Ag2-C8,C9 2.260(2), Ag2-N3 2.235(3), Ag2-C17 2.410(2), Ag2-C18 2.427(2), Ag2-C17,C18 2.301(2), C8-Ag2-N3 141.5(2), C8-Ag2-C17 137.0(3), C8-Ag2-C18 101.2(2), C9-Ag2-N3 109.2(2), C9-Ag2-C17 170.5(2), C9-Ag2-C18 134.7(2), C8,C9-Ag2-C17,C18 135.7(2), N3-Ag2-C17 80.3(2), N3-Ag2-C18 115.9(2), N3-Ag2-C17,C18 98.2(2).*

Both Ag1 and Ag2 are three coordinate. The bond angles measured around the environments of both silver atoms are similar. The largest bond angle measured between the centroids of the coordinated olefin groups is 135.1° for Ag1 and 135.7° for Ag2. The second largest bond angle is between the thiazole nitrogen atom and the centroid of the olefinic group of the adjacent ligand with 126.6° for Ag1 and 125.7° for Ag2. The third bond angle is

measured between the centroid of the olefin group and the chelated nitrogen atom of the thiazole ring with bond angles of 98.1° and 98.2° for Ag1 and Ag2, respectively. From this, the geometry of both Ag1 and Ag2 can be described as distorted trigonal planar. All the measured silver-carbon bond distances are within the expected bond distance range for silver-olefin interactions. The silver-nitrogen bond distances (Ag1-N1 2.205 Å and Ag2-N3 2.235 Å) are shorter than the corresponding distances measured in complexes **3.18**-**3.20**.

*3.2.6 Complex of 8-(N,N-diallylamino)quinoline (**3.16**)*

With silver(I) perchlorate (**3.23**)

Ligand **3.16** was mixed with two equivalents of silver(I) perchlorate in acetone. Diethyl ether diffusion into the reaction mixture allowed the growth of suitable crystals for X-ray crystal structure analysis. The structure was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand molecule, one silver atom, and a non-coordinated perchlorate anion revealing a 1:1 (metal:ligand) ratio or M_1L_1 type coordination complex, as shown in Figure 3.19.

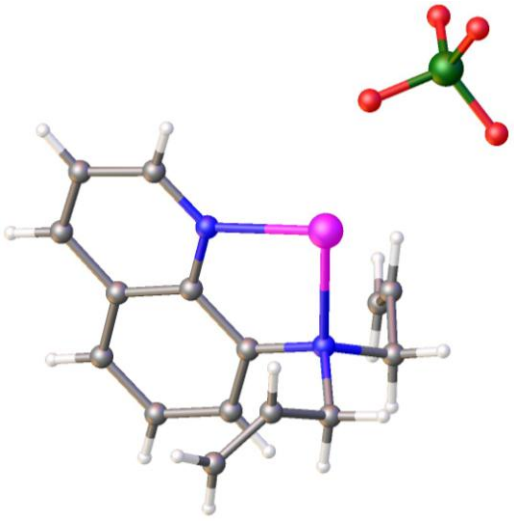


***Figure 3.19** – The asymmetric unit of complex **3.23**.*

The structure grows into a 1D polymeric assembly through the coordination of the olefin functional group of one of the allyl arms and the amine and quinoline nitrogen atoms of the ligand. The coordination of the amine nitrogen

observed in this complex, is unique throughout this project. The position of the quinoline nitrogen atom (N1) and the amine nitrogen (N2) of the diallylamine group is the main reason for the formation of a stable five membered chelate ring. The silver atom also coordinates to one allyl arm of an adjacent ligand, as shown in Figure 3.20. The presence of a non-coordinated alkene functional group is also another rare feature observed in this study. The nitrogen atoms of the ligand molecule chelate with silver, while the allyl arm bridges the adjacent silver atom. Therefore, ligand **3.16** acts in a tridentate chelating and bridging manner. The silver atom is three coordinate, with the largest bond angle measured between the centroid of the coordinated olefin group and the amine nitrogen (N2-Ag1-C14,C15) with a bond angle of 144.6°, the second one is between the centroid of the olefin group and the quinoline ring nitrogen atom (N1-Ag1-C14,C15) with a bond angle of 137.6°. The smallest angle is measured between the two nitrogen atoms (N1-Ag1-N2) with a bond angle of 76.7°. From these bond angle measurements, silver is a three coordinate metal atom with a severely distorted trigonal geometry.

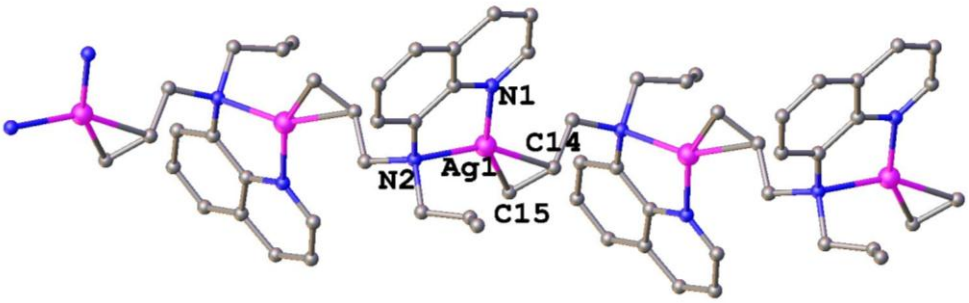


Figure 3.20 *– Part of the polymeric structure of complex* ***3.23****. All hydrogen atoms and the non-coordinated perchlorate anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N1 2.240(4), Ag1-N2 2.327(2), Ag1-C14 2.369(2), Ag1-C15 2.260(2), Ag1-C14,C15 2.206(2), N1-Ag1-N2 76.8(1), N1-Ag1-C14 120.7(2), N1-Ag1-C15 155.1(3), N1-Ag1-C14,C15 137.6(3), N2-Ag1-C14 158.3(3), N2-Ag1-C15 128.2(2), N2-Ag1-C14,C15 144.6(3).*

All the measured silver-carbon bond distances are in the expected range for silver-olefin interactions. The bond distances measured between silver and the nitrogen atoms are in the expected range; however, the Ag1-N1 bond distance (2.240 Å) is slightly shorter than the Ag1-N2 (2.327 Å) bond distance. The quinoline ring of the ligand alternates its position above and below the plane of the polymeric chain, which minimizes the opportunity of π-π interactions between the aromatic rings. Since the ligand bridges adjacent silver atoms through the interaction of one of the allyl arms and chelation of the two nitrogen atoms, the separation distance between adjacent silver atoms is 5.544 Å, which is shorter than that seen in complexes **3.18**-**3.22**.

3.2.7 Complexes of 4-(N,N-diallylamino)azobenzene (**3.17**)

Several attempts were made to grow crystals of complexes of ligand **3.17** with different silver(I) salts using different methods of crystal growth; however, to date no success has been achieved.

3.3 Ligands containing two diallylamine groups

Several attempts were made to investigate the coordination of ligands containing two diallylamine groups using the compounds shown in Figure 3.21.

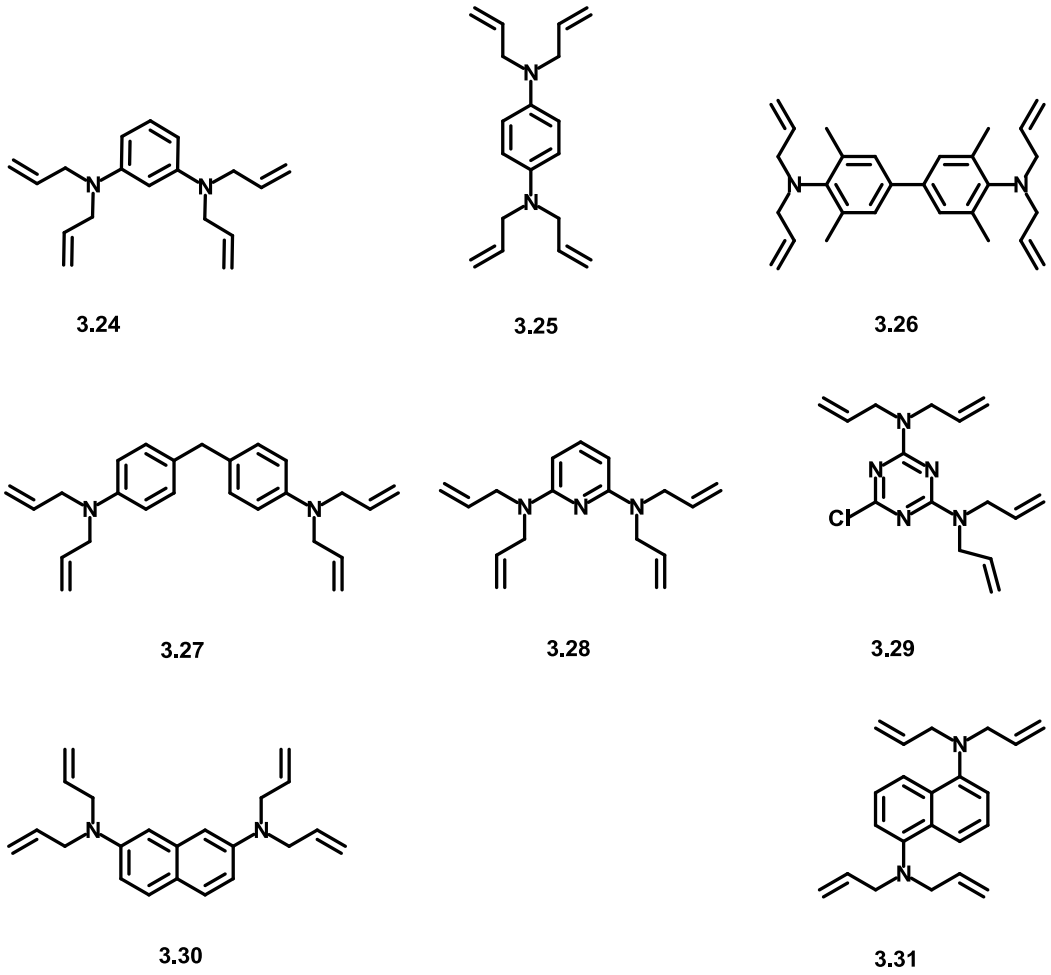
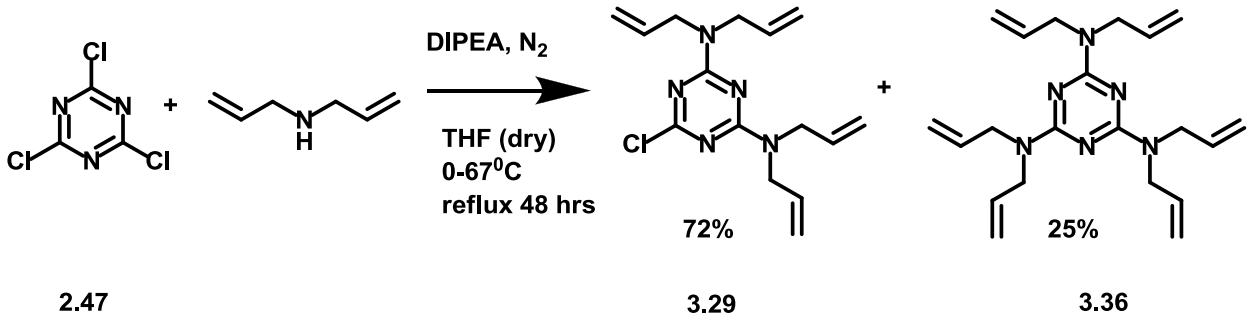


Figure 3.21 *– Compounds synthesised to investigate the interaction of silver with ligands containing two diallylamine groups.*

3.3.1 Synthesis of ligands containing two diallylamine groups

The synthetic method for these ligands, except for **3.29**, is the same. They were synthesised from their corresponding amines and allyl bromide under the reaction conditions shown in scheme 3.1. Ligand **3.29** was synthesised from diallylamine and cyanuric chloride under the conditions shown in scheme 3.2.[152]



Scheme 3.2 - Synthesis of ligand **3.29** from cyanuric chloride.

Ligand **3.29** displayed two decoalescences in both ^{13}C and ^{1}H NMR spectra, which doubled the number of signals of each carbon and proton in the allyl arms, as has been previously observed in Katritzky's work.[190] This is due to restricted rotation about the exocyclic C-N bonds in a molecule that lacks symmetry. Ligand molecules **3.24**, **3.26**, **3.28** and **3.30** are new compounds, while **3.25**,[151, 191] **3.27**,[192-193] **3.29**,[194-195] and **3.31**[196] are known compounds. All these ligands are oily liquids except for **3.26**, which crystallizes upon standing over a period of time. The crystal structure of **3.26** was solved in the monoclinic Cc space group and the structure is shown in Figure 3.22. The asymmetric unit contains two molecules. One of the allyl arms is disordered over two sites with 60% dominant position occupancy.

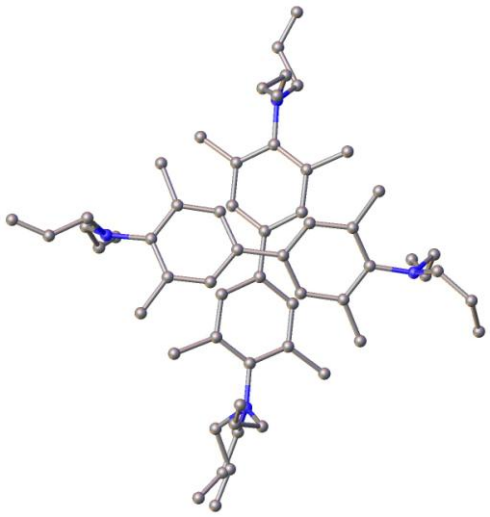


Figure 3.22 *– The structure of ligand* ***3.26****. All hydrogen atoms are omitted for clarity.*

In addition to the usual characterization methods, ligands **3.30** and **3.31** were further characterized by COSY and HSQC to assign all the carbon and proton signals.

*3.3.2 Attempts to grow crystals of complexes of N^1,N^1,N^3,N^3-tetraallyl-1,3-diaminobenzene (**3.24**) and N^2,N^2,N^6,N^6-tetraallyl-2,6-diaminopyridine (**3.28**)*

Encouraged by the results[173] from the reaction of **3.3** with $AgPF_6$ and $AgNO_3$ that resulted in the formation of polymeric structures and the results obtained using ligand **3.12** with $AgClO_4$, several attempts were made to grow crystals of silver(I) complexes with ligand **3.24**. When ligand **3.24** was mixed with any of the silver(I) salts (except silver nitrate) it formed a white precipitate, which was insoluble in most common solvents. Since silver nitrate is soluble in water the reaction with **3.24** is quite slow; but no crystals were obtained. Changing the solvent from acetone to toluene with silver triflate avoids the formation of a precipitate; however, it leads to the formation of an oily gummy material. Attempts to grow crystals of **3.24** with copper(I) and mercury(II) salts were also not successful.

The successful results of ligands **3.13** and **3.14** with silver was the basis to try to complex **3.28** with different silver(I) salts. The relationship between the diallylamine groups in **3.24** and **3.28** are the same, except that there is a pyridine ring in **3.28** and a benzene ring in **3.24**. From the similarity of the structures of these two ligands, we hoped that **3.28** might have a better coordination capacity with silver than **3.24**; however, all attempts to grow crystals of such complexes were not successful. Since the nitrogen atom of the heterocyclic ring is sterically hindered, attempts were made by changing the ratio from 1:2 and 1:3 (ligand:silver) to 1:10 (ligand:silver) ratio to grow crystals of complexes, as reported in the literature;[60] however, no success was achieved.

*3.3.3 Attempts to grow crystals of complexes of N^1,N^1,N^4,N^4-tetraallyl-1,4-diaminobenzene(**3.25**), $N^4,N^4,N^{4'},N^{4'}$-tetraallyl-4,4'-diamino-3,3',5,5'-tetramethylbiphenyl (**3.26**) and $N^4,N^4,N^{4'},N^{4'}$-tetraallyl-4,4'-diaminodiphenylmethane (**3.27**)*

In complex **3.18**, the coordination of the aromatic carbon atom *para* to the diallylamine group is believed to be the result of the electron donating character of the amine group towards the aromatic ring. This enhances the electron density of the aromatic ring, particularly to the carbon atom that coordinates in a η^1-manner with silver. From this point of view trying to react **3.25** with different silver(I) salts seemed to be an intriguing prospect. Indeed **3.25** reacted with different silver(I) salts but its reaction was too fast, which was visible by changing its colour to deep purple as soon as a drop of any silver(I) salt solution was added. Attempts were made by diluting the solution to the 10^{-6} M range but through slow evaporation of the solvent the usual deep purple solution was consistently obtained. Several attempts were made with different copper(I), zinc(II) and mercury(II) salts; but no growth of crystals of the complexes was achieved. In hoping to slow down the fast reaction of ligand **3.25** with silver, two drops of perchloric acid were mixed with the ligand followed by the addition of two equivalents of the solution of $AgClO_4$ in acetone. Diethyl ether diffusion was allowed into the reaction mixture, which resulted in the growth of needle shaped crystals within an hour. The structure was solved in the monoclinic $P2_1/n$ space group, revealing a perchlorate salt **3.25a** without any coordination of silver, as shown in Figure 3.23. The asymmetric unit contains half a protonated ligand molecule and a disordered perchlorate anion, over two sites with 78% dominant position occupancy.

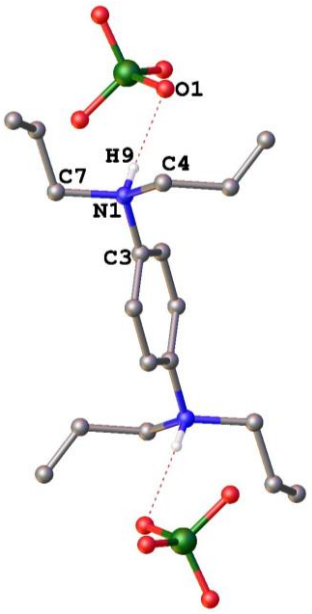


Figure 3.23 *– The perchlorate salt of ligand* ***3.25*** *showing the position of the proton attached to the amine group. The disorder of the perchlorate anion and hydrogen atoms, except those attached to nitrogen, are removed for clarity. Selected bond lengths (Å) and angles (°): N1-H9 0.830(3), N1-C3 1.476(3), N1-C4 1.522(3), N1-C7 1.516(3), C3-N1-H9 106.0(2), C3-N1-C4 113.1(2), C3-N1-C7 111.2(2), H9-N1-C4 105.0(2), H9-N1-C7 108.0(2).*

The perchlorate anion has a hydrogen bonding interaction[197-198] with the hydrogen atom (H9) on the protonated amine group with bond distance and angles shown in table 3.2.

D-H···A	D-H	H···A	D···A	D-H···A
N1-H9···O1	0.830	2.054	2.862	164.30

Table 3.2 *Hydrogen bonding geometry between the perchlorate anion and the proton from the amine group.*

After all these failed attempts to crystallize complexes of ligand **3.25**, we thought that increasing the separation distance between the diallylamine

groups might help to grow crystals of silver(I) complexes. Ligand **3.26** has a rigid biphenyl core structure, which minimizes the flexibility of the ligand, while the distance between the diallylamine groups increases relative to **3.25**. Several attempts were made to grow crystals of different silver(I) salts with ligand **3.26**, using different solvents and crystal growth methods from the usual diethyl ether diffusion into the reaction mixture, slow evaporation of the solvent, using H-tube and U-tubes, but no success was achieved.

Further increment of the separation distance between the diallylamine groups was attempted by using ligand **3.27** that has a methylene group between the two phenyl rings. The introduction of this methylene group not only increases the separation distance between the diallylamine groups but also introduces some flexibility; however, all the attempts were unsuccessful with this ligand as well.

*3.3.4 Attempts to grow crystals of complexes of N^2,N^2,N^7,N^7-tetraallyl-2,7-diaminonaphthalene (**3.30**) and N^1,N^1,N^5,N^5-tetraallyl-1,5-diaminonaphthalene (**3.31**)*

Another way to alter the separation distance between the donor groups is to change the core structure. Changing the core structure from a benzene ring to naphthalene not only increases the separation between the coordination sites but also increases the potential for η^2 arene-silver(I) coordination. Since any electron cloud perturbation introduced by the coordination of silver(I) can spread over two ring systems in naphthalene, the potential of the η^2 arene-silver(I) coordination increases.[120] Ligand **3.30** is the diallylamine version of **3.5**, which produced 1D-coordination polymers with $AgBF_4$ and $AgPF_6$.[173] Attempts were made to grow crystals of complexes of **3.30** with $AgClO_4$, $AgBF_4$, $Ag(SO_3CF_3)$ and $AgPF_6$ without any success. Similar attempts were made with ligand **3.31**, but no successful growth of a silver(I) complex was achieved. However in an attempt to grow crystals of a $AgClO_4$ complex with **3.31**, crystals of an ammonium perchlorate salt (**3.31a**) were obtained. The structure of **3.31a** was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains one perchlorate anion and half of a protonated

ligand molecule. The perchlorate anion has hydrogen bonding with the protonated amine group, as shown in Figure 3.24.

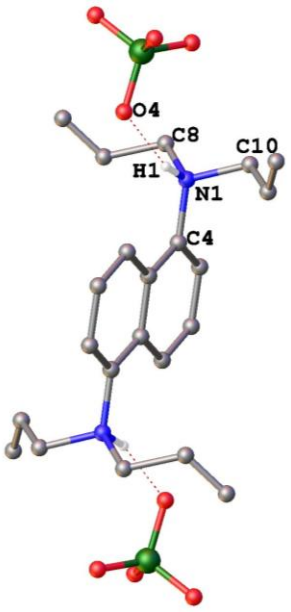


Figure 3.24 *- The perchlorate salt of ligand* ***3.31*** *showing the position of the proton attached on the protonated amine group. Selected bond lengths (Å) and angles (°): C4-N1 1.482(2), C8-N1 1.523(2), C10-N1 1.529(2), H1-N1 0.881(2), C4-N1-C8 112.8(1), C4-N1-C10 112.1(1), C4-N1-H1 111.5(1), C8-N1-C10 110.2(1), C8-N1-H1 103.3(1), C10-N1-H1 106.9(2).*

Interestingly, the diallylamine arms are perpendicular to the plane of the naphthalene ring. All the measured bond angles are very close to the tetrahedral arrangement with the largest measured angle being 112.0°. The perchlorate anion has a hydrogen bonding interaction[197-198] with the hydrogen atom (H1) from the amine group with bond distance and angles shown in table 3.3.

D-H···A	D-H	H···A	D···A	D-H···A
N1-H1···O4	0.881	2.055	2.906	162.19

Table 3.3 *Hydrogen bonding geometry between the perchlorate anion and the proton from the amine group.*

*3.3.5 Complexes of 2,4-bis(diallylamino)-6-chloro-1,3,5-triazine (**3.29**)*

With silver(I) perchlorate (**3.32**)

Ligand **3.29** was mixed with two equivalents of silver(I) perchlorate solution in acetone. As soon as the two components were mixed, a white precipitate was formed. This precipitate was dissolved in water and slow evaporation resulted in the growth of tiny crystals. The crystal structure was solved in the triclinic P-1 space group. The asymmetric unit contains one full ligand molecule, two silver atoms, a coordinated water molecule, a non-coordinated acetone molecule and two non-coordinated perchlorate counter anions, revealing a 1:2 (ligand:metal) ratio complex, as shown in Figure 3.25. The structure grows into a tetranuclear discrete assembly through the coordination of two ligand molecules with four silver atoms using all of the allyl arms and the three triazine ring nitrogen atoms to form an M_4L_2 coordination complex.

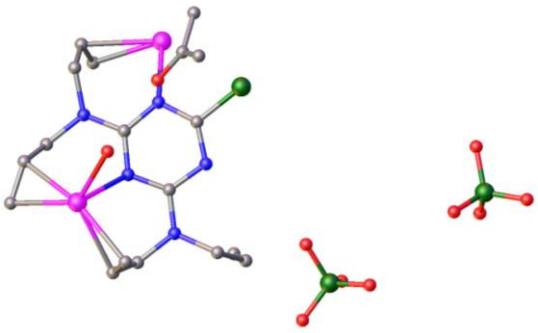


Figure 3.25 *– The asymmetric unit of complex **3.32**. All hydrogen atoms have been omitted for clarity.*

As shown in Figure 3.26, there are two crystallographically independent silver atoms, each with coordination number four. Ag1 bridges two adjacent ligand

molecules through the coordination of two allyl arms (C8A=C9A and C11=C12) and two nitrogen atoms from triazine rings (N1A and N3) of adjacent ligands. Ag2 bridges two diallylamines by coordinating with two allyl arms (C5=C6 and C14=C15) of the same ligand, a nitrogen atom of the triazine ring (N2) and a water molecule (O9).

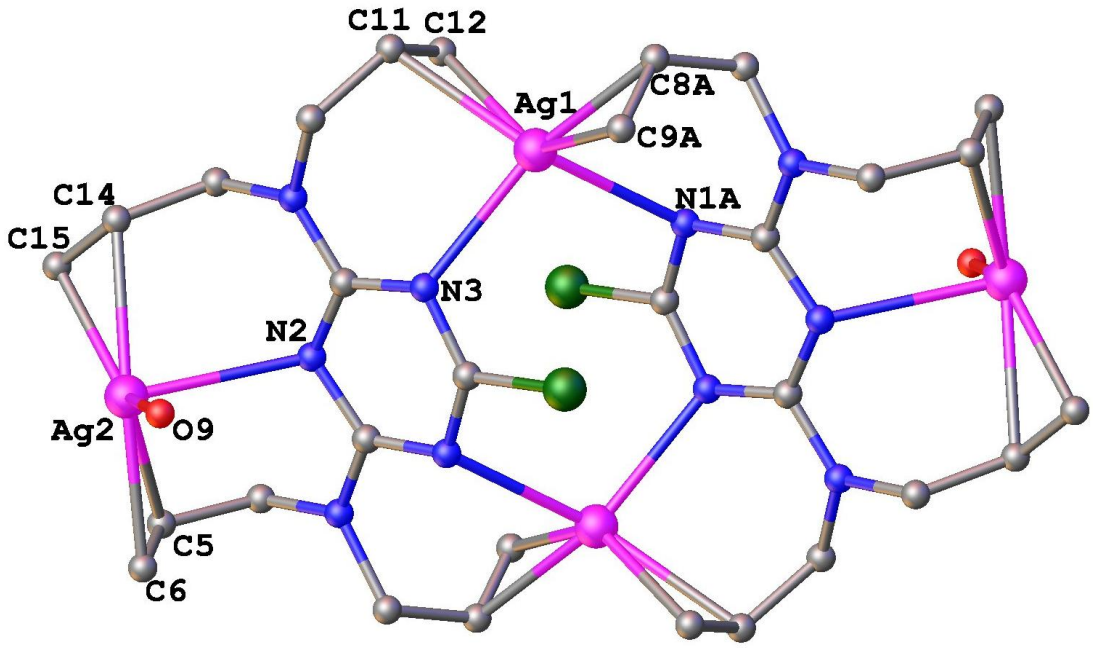


Figure 3.26 *– The tetranuclear M_4L_2 discrete assembly of complex* ***3.32****. All hydrogen atoms, the non-coordinated acetone molecules and the perchlorate counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°):Ag1-C8A 2.407(3), Ag1-C9A 2.405(3), Ag1-C8A,C9A 2.311(3), Ag1-N3 2.408(3), Ag1-N1A 2.537(3), Ag1-C11 2.452(3), Ag1-C12 2.451(3), Ag1-C11,C12 2.360(3), N3-Ag1-C11 85.1(1), N3-Ag1-C12 92.1(1), N3-Ag1-C11,C12 88.6(1), N3-Ag1-N1A 99.2(2), N3-Ag1-C8A 150.6(2), N3-Ag1-C9A 118.4(2), N3-Ag1-C8A,C9A 134.5(2), C11-Ag1-N1A 141.0(2), C12-Ag1-N1A 109.6(2), C11,C12-Ag1-N1A 125.3(2), C11-Ag1-C8A 110.8(2), C11-Ag1-C9A 119.2(2), C12-Ag1-C8A 114.5(2), C12-Ag1-C9A 138.9(2), C8A,C9A-Ag1-C11,C12 122.9(2), N1A-Ag1-C8A 84.2(1), N1A-Ag1-C9A 93.0(1), N1A-Ag1-C8A,C9A*

88.5(1), Ag2-O9 2.333(3), Ag2-N2 2.627(3), Ag2-C5 2.498(4), Ag2-C6 2.400(4), Ag2-C5,C6 2.357(4), Ag2-C14 2.437(4), Ag2-C15 2.366(4), Ag2-C14,C15 2.306(4), O9-Ag2-N2 91.4(1), O9-Ag2-C5 124.7(2), O9-Ag2-C6 96.6(1), O9-Ag2-C5,C6 111.1(2), O9-Ag2-C14 105.6(2), O9-Ag2-C15 132.4(1), O9-Ag2-C14,C15 119.2(2), N2-Ag2-C5 79.7(1), N2-Ag2-C6 93.7(1), N2-Ag2-C5,C6 86.4(2),N2-Ag2-C14 79.6(2), N2-Ag2-C15 97.1(2), N2-Ag2-C14,C15 88.2(2), C5-Ag2-C14 125.5(2), C5-Ag2-C15 103.0(2), C6-Ag2-C14 157.0(2), C6-Ag2-C15 129.4(2), C5,C6-Ag2-C14,C15 129.6(2).

Interestingly, no two allyl arms from a single diallylamine group coordinate with the same silver atom. The allyl arms bridge Ag1 and Ag2 in a “trans-mode” of coordination. The two crystallographically independent silver atoms (Ag1 and Ag2) are doubly bridged by the ligand with a separation distance of 6.620 Å.

In the Ag1 environment, the largest angle is formed between one of the triazine nitrogen atoms (N3) and the centroid of (C8A=C9A) with a bond angle of 134.5°. The second largest angle is formed between the second nitrogen atom of the triazine ring (N1A) and the centroid of (C11=C12) with a bond angle of 125.3°. The calculated τ_4 value for Ag1 is 0.71 this being a seesaw geometry.

The largest bond angle measured in the Ag2 environment is between the centroids of the coordinated olefinic groups (C5=C6 and C14=C15) with a bond angle of 129.6°. The second largest bond angle is between the coordinated water molecule (O9) and the centroid of (C14=C15). The calculated τ_4 value for Ag2 is 0.79, revealing a seesaw geometry.

An interesting feature of this structure is the pyrimidalization of the triazine ring nitrogen atoms, which have long silver-nitrogen bond distances. The measured distance between Ag1-N3 (2.408 Å) and Ag1-N1A (2.537 Å) are longer than most of the reported bond distances for silver-N-heterocyclic ring interactions[132, 153] but shorter than the distance measured between Ag2-N2

2.627 Å. The distance measured between Ag2-N2 is shorter than the literature bond distances for similar silver-triazinyl nitrogen interactions.[187-188] All the silver-carbon bond distances are in the expected range for olefinic carbon-silver interactions. The coordination of the three triazine ring nitrogen atoms, as well as the diallyl arms of the ligand, positions the chlorine atoms far from each other but in a parallel and close distance to the triazine ring for halogen-π interactions. The measured distance between the centroid of the triazine ring to chlorine atom is 3.259 Å, which is shorter than the reported distance for such types of interactions in the literature(3.4-3.8 Å).[199]

Hydrogen bonding between the coordinated water molecule and the perchlorate anion contributes further stabilization of the tetranuclear dimeric structure of the complex. The ligand molecule acts as a heptadentate ligand by coordinating through the three nitrogen atoms of the triazine ring and the four allyl arms.

With silver(I) triflate (**3.33**)

Ligand **3.29** was mixed with two equivalents of silver(I) triflate in acetone. As soon as the two components were mixed, a white precipitate was formed. This was dissolved in water and slow evaporation of the solvent afforded crystals after two weeks. The structure was solved in the trigonal R-3 space group. The asymmetric unit contains one full ligand molecule, two silver atoms, one coordinated and one non-coordinated triflate counter anion, as shown in Figure 3.27. Similar to complex **3.32**, the structure grows into a tetranuclear dimeric discrete assembly or an M_4L_2 type coordination complex; however, in complex **3.33** only two of the triazine nitrogen atoms coordinate to silver.

There are two crystallographically independent silver atoms (Ag1 and Ag2). Ag1 is four coordinate through the coordination of two allyl arms and two triazine nitrogen atoms from adjacent ligands. The largest bond angle around Ag1 environment is measured between the coordinated triazine nitrogen atom and the centroid of the coordinated olefin group (N1-Ag1-C8A=C9A) with a bond angle of 128.4°. The second largest angle is also measured between the other coordinated triazine nitrogen atom (N3A) and the centroid of the olefin

group (C11=C12) with a bond angle of 127.1°, as shown in Figure 3.28. The calculated τ_4 value for Ag1 is 0.74, revealing a seesaw shape.

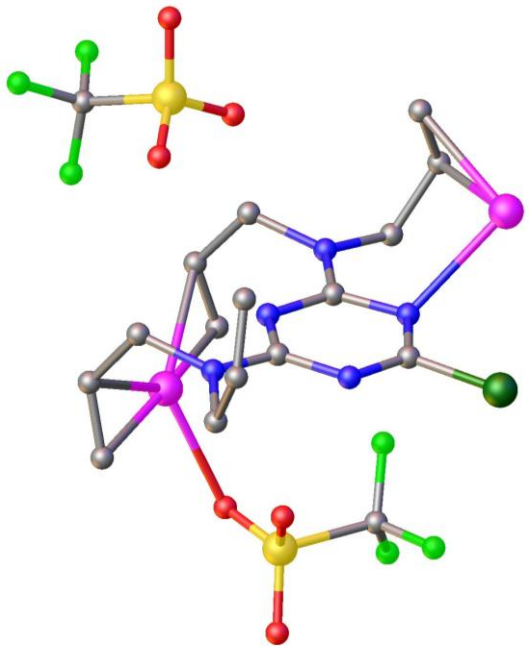


Figure 3.27 *– The asymmetric unit of complex* ***3.33****. All hydrogen atoms have been omitted for clarity.*

The silver-nitrogen bond distances (Ag1-N3A 2.414 Å) and (Ag1-N1 2.445Å) are a little bit longer than the usual silver-N-heterocyclic bond distances but shorter than some of the long silver-triazinyl nitrogen atom distances measured in complex **3.32**. Ag1 is bridging two ligands through chelation of an allyl group and a triazinyl nitrogen atom from the same ligand.

Unlike complex **3.32**, Ag2 is three coordinate through the coordination of a triflate counter anion and two allyl arms from adjacent diallylamine groups of the same ligand. The largest bond angle (150.4°) is measured between the centroids of the two coordinated olefin groups (C5,C6-Ag2-C14,C15) with a distorted trigonal geometry. There is a weak interaction between Ag2 and N2 with a separation distance of 2.670 Å, which is longer than the distance measured in complex **3.32** and also in the literature for similar structures.[187-188] As shown in the asymmetric unit, the coordination of the allyl arms from the same diallylamine group are in a “trans-mode”. Similar to complex **3.32**, there is also a halogen-π interaction between the chlorine atom and the

centroid of the triazine ring with a separation distance of 3.351 Å, which is longer than the distance measured in complex **3.32** (3.259 Å), but shorter than those reported in the literature.[199]

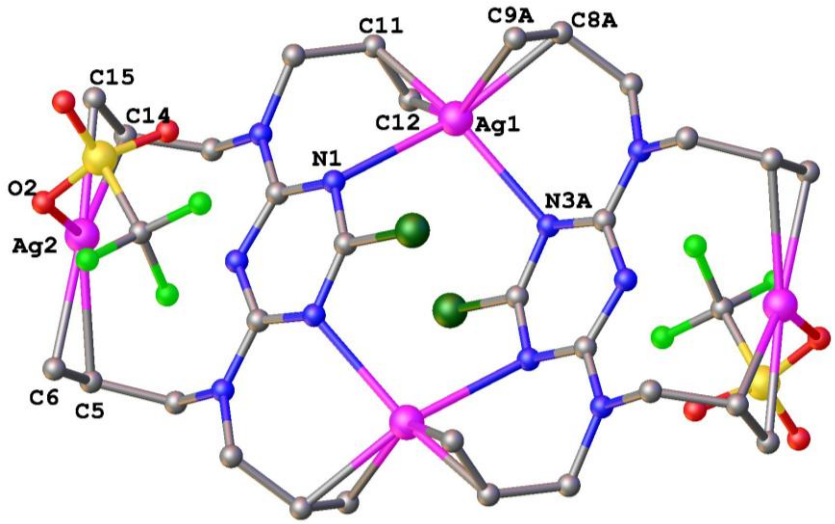


Figure 3.28 *– The tetranuclear dimeric discrete assembly of complex* ***3.33****. All hydrogen atoms and the non-coordinated triflate counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N3A 2.414(4), Ag1-C8A 2.415(2), Ag1-C9A 2.451(2), Ag1-C8A,C9A 2.337(2), Ag1-N1 2.445(4), Ag1-C11 2.414(1), Ag1-C12 2.438(1), Ag1-C11,C12 2.332(1), N3A-Ag1-C8A 87.2(2), N3A-Ag1-C9A 96.0(2), N3A-Ag1-C8A,C9A 91.7(2), N3A-Ag1-C11 143.2(2), N3A-Ag1-C12 111.3(2), N3A-Ag1-C11,C12 127.1(2), C8A-Ag1-N1 144.7(1), C9A-Ag1-N1 112.7(1), N1-Ag1-C8A,C9A 128.5(1), C8A-Ag1-C11 107.6(2), C8A-Ag1-C12 115.0(2), C9A-Ag1-C11 114.6(2), C9A-Ag1-C12 137.6(2), C8A,C9A-Ag1-C11,C12 120.7(2), N1-Ag1-C11 85.5(2), N1-Ag1-C12 93.6(2), N1-Ag1-C11,C12 89.5(2), Ag2-C5 2.535(1), Ag2-C6 2.395(1), Ag2-C5,C6 2.374(1), Ag2-C14 2.505(2), Ag2-C15 2.424(2), Ag2-C14,C15 2.373(2), Ag2-O2 2.410(4), C5-Ag2-C14 120.1(2), C5-Ag2-C15 151.2(2), C6-Ag2-C14 151.0(2), C6-Ag2-C15 173.5(2), C5,C6-Ag2-C14,C15 150.4(2), C5-Ag2-O2 116.0(2), C6-Ag2-O2*

85.4(2), C5,C6-Ag2-O2 101.2(2), C14-Ag2-O2 123.6(2), C15-Ag2-O2 92.8(2), C14,C15-Ag2-O2 108.5(2).

The separation distance between the doubly bridged silver atoms (Ag1 and Ag2) is 6.642 Å, which is quite silmilar to that measured in complex **3.32**. Ligand **3.29** coordinates through six donating groups with silver in a hexadentate manner. No chelation of allyl arms from the same diallylamine group was observed.

In general, the coordination of the ligand **3.29** is both chelating and bridging as represented by Figure 3.29. The long and weak triazine nitrogen coordination with silver is represented by a hollow arrowhead.

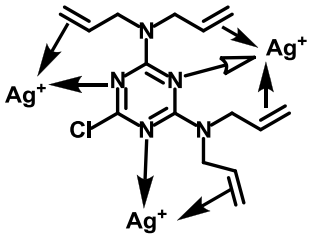
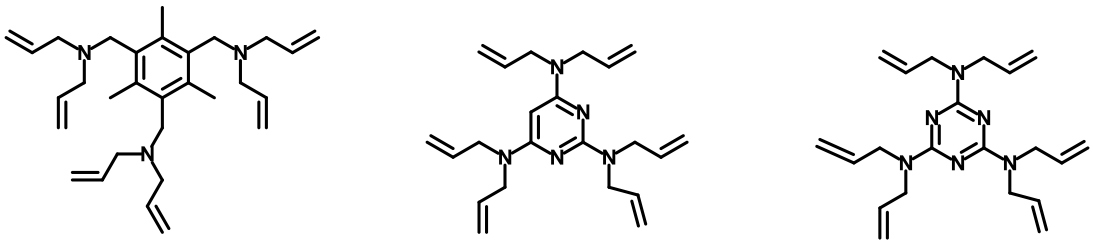


Figure 3.29 *– Simple representation of the binding modes of ligand* ***3.29*** *with silver.*

3.4 Ligand molecules containing three diallylamine groups

Attempts were made to investigate the coordination of ligand molecules containing three diallylamine groups with silver. Ligands synthesised for this study have different core structures, as shown in Figure 3.30.

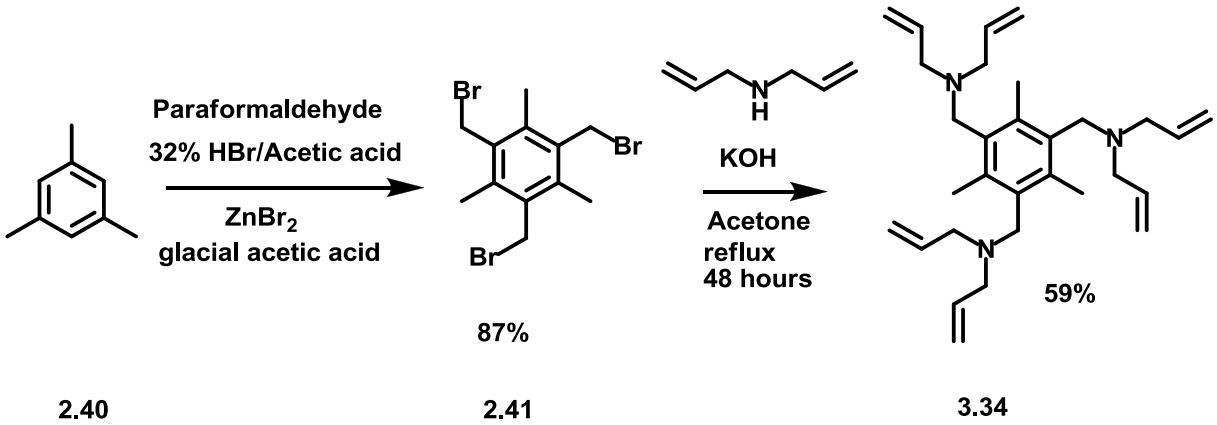


3.34 **3.35** **3.36**

Figure 3.30 *– Ligands used to investigate the coordination chemistry of silver with ligands containing three diallylamine groups.*

3.4.1 Synthesis of the ligand molecules

Ligand **3.34** is a known compound,[200] however, the synthesis and characterisation of this molecule was not reported. Recently, the same group reported another result using this ligand, in which the ligand was characterised by mass spectrometry and infrared spectroscopy.[201] Ligand **3.34** was synthesised in two steps from 1,3,5-trimethylbenzene under the conditions shown in scheme 3.3.



Scheme 3.3 - Synthesis of ligand **3.34** from 1,3,5-trimethylbenzene.

Ligand **3.35** was synthesised from 2,4,6-triaminopyrimidine and allylbromide under similar conditions to those shown in scheme 3.1. Ligand **3.36** was synthesised under the conditions shown in scheme 3.2. Both **3.35**[202] and **3.36**[203] are known compounds.

*3.4.2 Complexes of N^1,N^1,N^3,N^3,N^5,N^5-hexaallyl-1,3,5-triaminomethyl-2,4,6-trimethylbenzene (**3.34**)*

Several attempts were made to grow crystals of complexes of different silver(I) salts with ligand **3.34**, including the method mentioned in the literature for their Cu(I)-olefin organometallic oligomers.[200] However, to date no success has been achieved to grow crystals suitable for X-ray structure analysis.

*3.4.3 Complex of 2,4,6-tris(diallylamino)pyrimidine (**3.35**)*

With silver(I) triflate (**3.37**)

Ligand **3.35** was mixed with three equivalents of silver(I) triflate solution in acetone. As soon as the ligand was added to the silver(I) triflate solution, a white precipitate was formed. This was dissolved in dichloromethane, followed by diethyl ether diffusion into the reaction mixture, which resulted in the growth of crystals suitable for X-ray structure study. The structure was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains two crystallographically independent complex molecules. Each complex has one full ligand molecule, one coordinated and another non-coordinated triflate counter anion, revealing a 1:2 (ligand:metal) ratio complex, as shown in Figure 3.31. In the asymmetric unit, one of the complexes has the triflate counter anion coordinated through one oxygen atom, while the other counter anion bridges through two oxygen atoms.

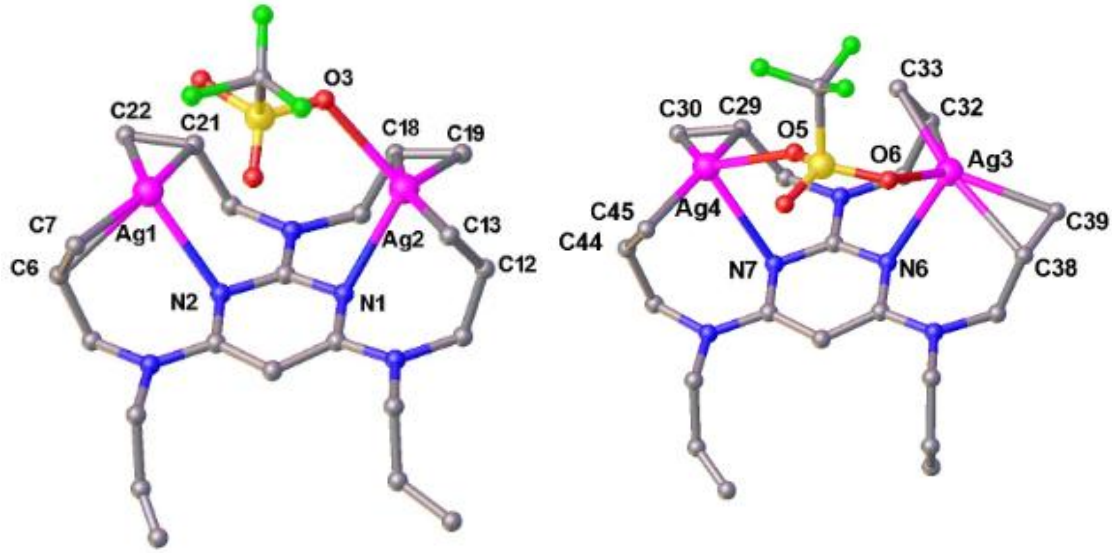


***Figure 3.31** – The asymmetric unit of complex **3.37** showing the two independent complexes. The non-coordinated triflate counter anions and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N2 2.478(4), Ag1-C6,C7 2.291(1), Ag1-C21,C22 2.283(2), N2-Ag1-C6,C7 91.2(1), N2-Ag1-C21,C22 95.4(2), C6,C7-Ag1-C21,C22*

136.1(2), Ag2-N1 2.482(4), Ag2-O3 2.391(2), Ag2-C12,C13 2.287(2), Ag2-C18,C19 2.335(2), N1-Ag2-O3 112.0(2), N1-Ag2-C12,C13 91.3(1), N1-Ag2-C18,C19 91.5(1), O3-Ag2-C12,C13 123.1(3), O3-Ag2-C18,C19 100.7(3), C12,C13-Ag2-C18,C19 131.1(3), Ag3-N6 2.530(4), Ag3-O6 2.390(4), Ag3-C32,C33 2.334(2), Ag3-C38,C39 2.327(2), N6-Ag3-O6 90.9(1), N6-Ag3-C32,C33 89.1(2), N6-Ag3-C38,C39 93.1(2), O6-Ag3-C32,C33 119.7(2), O6-Ag3-C38,C39 107.0(2), C32,C33-Ag3-C38,C39 133.1(2), Ag4-N7 2.637(4), Ag4-C29 2.437(2), Ag4-C30 2.400(2), Ag4-C44 2.427(2), Ag4-C45 2.407(2), Ag4-O5 2.319(4), N7-Ag4-O5 81.6(1), N7-Ag4-C29,C30 85.9(2), N7-Ag4-C44,C45 88.1(2), O5-Ag4-C29,C30 119.3(2), O5-Ag4-C44,C45 110.2(2), C29,C30-Ag4-C44,C45 128.6(2).

No allyl arms from the same diallylamine group are chelated with a silver atom. The diallylamine arm coordinated through both of the allyl arms has a “cis-mode” of coordination with silver. The other two diallylamine groups contain a coordinated and a non-coordinated allyl arm. The coordinated allyl arms are above the plane of the pyrimidine ring, while the non-coordinated ones are below the plane of the pyrimidine ring this being a “trans-mode” of coordination. All the allyl arms beside the pyrimidine nitrogen atoms of the N-heterocyclic ring are coordinated with silver, while the allyl arms remote from the pyrimidine ring nitrogen atom are not coordinated.

The pyrimidine nitrogen atoms are also coordinated with silver; however, the bond length for the silver-pyrimidinyl nitrogen atoms are longer than the pyrimidinyl nitrogen-silver bond distances measured in other work. From the two complex structures, the Ag3-N6 bond distance (2.530 Å) and Ag4-N7 (2.637 Å) are longer than the Ag1-N2 (2.478 Å) and Ag2-N1 (2.482 Å). Although these silver-nitrogen interactions are weak and long (especially Ag3-N6 and Ag4-N7), it seems that they are influential on the coordination of the allyl arms with silver. Ag3 and Ag4, are also bridged by the triflate anion. Ag2 is also coordinated with a triflate anion; however, no coordination of Ag1 with the triflate counter anion is observed. All the silver-oxygen bond distances

observed (Ag2-O3 2.391, Ag3-O6 2.390, Ag4-O5 2.319 Å) are in the expected range for such types of interactions. All the silver-carbon bond distances are in the expected range for silver-olefin interactions.

The ligand bridges Ag1·····Ag2 with a separation distance of 4.976 Å, while the Ag3···Ag4 separation distance is 5.147 Å. Clearly both structures are M_2L_1 type discrete assemblies with very high pyrimidalization of the pyrimidine ring nitrogen atoms. Since the coordination of the triflate counter anion with silver atoms in both structures is different they have some differences.

Ag1 is three coordinate with the largest bond angle between the centroids of the olefins (C6,C7-Ag1-C21,C22 136.1°), the second and third angles are between the pyrimidine nitrogen (N2) and the centroids of the olefins with bond angles 91.1° and 95.4°, which results in a severely distorted trigonal planar geometry.

Ag2 is four coordinate with the largest bond angle being between the centroids of the olefins (C12,C13-Ag2-C18,C19 131.1°) and the second largest angle is between the oxygen atom of the triflate anion (O3) and the centroid of one of the coordinated olefins (C12=C13) with a bond angle (O3-Ag2-C12,C13 123.1°). The calculated τ_4 value is 0.75, revealing a seesaw shape.

Ag3 is four coordinate with the largest angle being between the centroids of the coordinated olefins (C32,C33-Ag3-C38,C39 133.1°) and the second largest angle is between one of the coordinated oxygen atoms of the triflate anion (O6) and the centroid of the alkene (C32=C33) with a bond angle 119.7°. The calculated τ_4 value is 0.76, again revealing a seesaw shape.

Ag4 is also four coordinate with the largest angle between the centroids of the coordinated olefins (C29,C30-Ag4-C44,C45 128.6°) and the second largest bond angle between one of the coordinated oxygen atoms of the triflate counter anion (O5) and the centroid of C29=C30 with a bond angle of 119.3°, which gives a calculated τ_4 value of 0.80, revealing trigonal pyramidal shape.

In general, the ligand acts as a hexadentate molecule by coordinating through six coordination sites out of eight possible ones. In addition to this, ligand **3.35** showed the advantage of using heterocyclic ring cores for better coordination of the allyl arms with silver, even though the silver-N-heterocyclic ring nitrogen interaction is weak and long.

*3.4.4 Complexes of 2,4,6-tris(diallylamino)-1,3,5-triazine (**3.36**)*

With silver(I) perchlorate (**3.38**)

Ligand **3.36** was mixed with three equivalents of silver(I) perchlorate in acetone. Diethyl ether diffusion into the reaction mixture afforded crystals suitable for X-ray crystal structure analysis. The structure was solved in the orthorhombic $P2_12_12_1$ space group. The asymmetric unit contains two ligand molecules, four silver atoms, one coordinated and three non-coordinated perchlorate anions, revealing a 1:2 (ligand:metal) ratio complex, as shown in Figure 3.32.

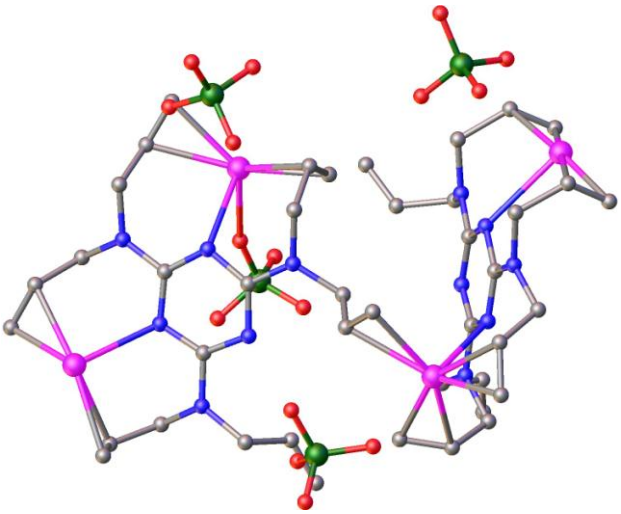
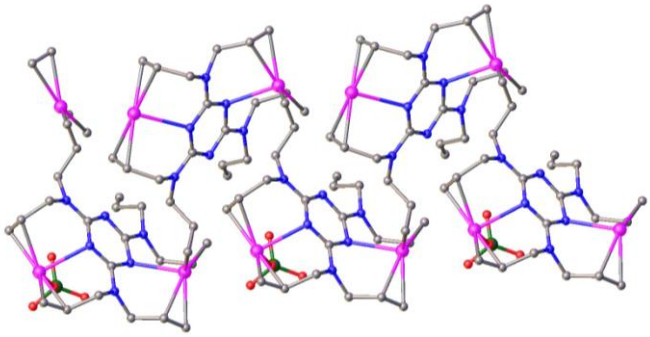


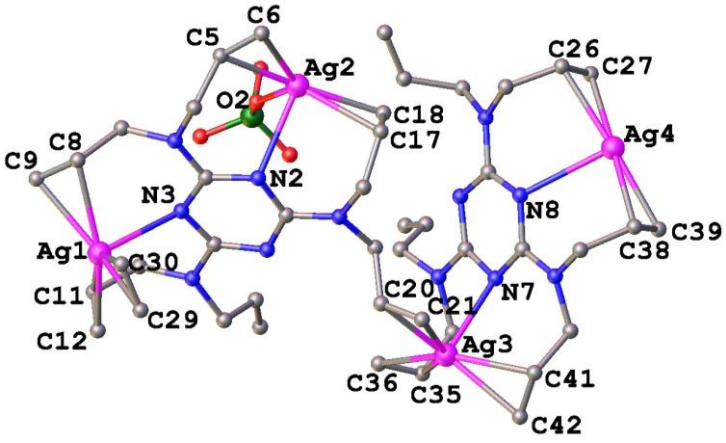
***Figure 3.32** – The asymmetric unit of complex **3.38**. All hydrogen atoms are omitted for clarity.*

The structure grows into a 1D polymeric assembly through the coordination of five allyl arms out of six and two triazinyl nitrogen atoms out of three of the triazine ring. Depending on the number of olefins coordinated with a single silver atom there are two types of coordinated silver atoms; those silver atoms

coordinated with three olefins (Ag1 and Ag3) and silver atoms coordinated with two olefins (Ag2 and Ag4). No two allyl arms from the same diallylamine group chelate with a single silver atom, rather the coordinated allyl arms are either from adjacent diallylamine groups or adjacent ligands. Due to this type of coordination of the allyl arms Ag1 and Ag3 bridge adjacent ligands, while Ag2 and Ag4 bridges adjacent diallylamine groups. Ag1, Ag2 and Ag3 are four coordinate while Ag4 is three coordinate, as shown in Figure 3.33.



A)



B)

Figure 3.33 *– A) Part of the 1D zigzag polymeric structure of complex* ***3.38****. B) Part of the polymeric assembly of complex* ***3.38*** *showing the labels of coordinated atoms. All hydrogen atoms and non-coordinated perchlorate anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N3 2.486(3), Ag1-C8 2.471(2), Ag1-C9 2.442(2),Ag1-C8,C9 2.363(2), Ag1-C11 2.462(2), Ag1-C12 2.378(2), Ag1-C11,C12*

2.331(2), Ag1-C29 2.518(2), Ag1-C30 2.387(2), Ag1-C29,C30 2.359(2), N3-Ag1-C8,C9 92.2(2), N3-Ag1-C11,C12 90.5(2), N3-Ag1-C29-C30 101.2(2), C8,C9-Ag1-C11,C12 128.6(2), C8,C9-Ag1-C29,C30 111.9(2), C11,C12-Ag1-C29,C30 117.8(2). Ag2-N2 2.527(4), Ag2-C5 2.389(1), Ag2-C6 2.387(1), Ag2-C5,C6 2.30(1), Ag2-O2 2.519(2), Ag2-C17 2.462(1), Ag2-C18 2.332(1), Ag2-C17,C18 2.313(1), N2-Ag2-O2 77.7(2), N2-Ag2-C5,C6 95.8(2), N2-Ag2-C17,C18 89.8(2), O2-Ag2-C5,C6 113.6(3),O2-Ag2-C17,C18 108.6(3), C5,C6-Ag2-C17,C18 137.6(2). Ag3-N7 2.501(3), Ag3-C20 2.515(2), Ag3-C21 2.411(2), Ag3-C20,C21 2.373(2), Ag3-C35 2.477(1), Ag3-C36 2.381(1), Ag3-C35,C36 2.338(1), Ag3-C41 2.473(2), Ag3-C42 2.444(2), Ag3-C41,C42 2.369(2), N7-Ag3-C20,C21 105.1(2), N7-Ag3-C35,C36 89.9(2), N7-Ag3-C41,C42 91.1(2), C20,C21-Ag3-C41,C42 112.3(2), C20,C21-Ag3-C35,C36 119.0(2), C35,C36-Ag3-C41,C42 127.4(2). Ag4-N8 2.630(4), Ag4-C26 2.426(1), Ag4-C27 2.351(1), Ag4-C26,C27 2.296(1), Ag4-C38 2.392(2), Ag4-C39 2.339(2), Ag4-C38,C39 2.273(2), N8-Ag4-C26,C27 89.3(2), N8-Ag4-C38,C39 87.8(2), C26,C27-Ag4-C38,C39 175.7(2).

All the coordinated allyl arms from the same diallylamine are in a “trans-mode” of coordination, which is above and below the plane of the triazine ring of the ligand. The same goes for the coordinated nitrogen atoms of the triazine ring. One of them coordinates above the plane of the ring, while the other is below the ring.

Ag1 is four coordinate with the coordination of three allyl arms and one nitrogen atom from the triazine ring. Two of the coordinated allyl arms are from two different diallylamine groups of the same ligand and the third one is from the adjacent ligand. The largest and the second largest bond angles around Ag1 are between the centroids of the coordinated olefins (C8,C9-Ag1-C11,C12 and C11,C12-Ag1-C29,C30) with bond angles 128.6° and 117.8°, respectively. The calculated τ_4 value for Ag1 is 0.81, revealing a trigonal pyramidal shape. All the silver-carbon bond lengths measured are in the

expected range for silver-olefin carbon interactions. The bond length of Ag1-N3 is 2.486 Å, which is longer than the silver-N-heterocyclic nitrogen bond distances, but shorter than other silver-nitrogen bond lengths measured in this structure.

Ag2 is four coordinate through the coordination of two allyl arms from the same ligand but different diallylamine groups, one nitrogen atom of the triazine ring and a perchlorate anion. The largest bond angle is measured between the centroids of the olefins (C5,C6-Ag2-C17,C18) with a bond angle of 137.6° and the second largest angle is measured between the oxygen atom of the perchlorate anion and the centroid of (O2-Ag2-C5,C6) with a bond angle of 113.6°. The calculated τ_4 value is 0.77, which revealed a seesaw shape for Ag2.

Ag3 is also four coordinate through the coordination of three allyl arms and one nitrogen atom of the triazine ring. Two of the three coordinated allyl arms are from the same ligand but different diallylamine groups and the third one is from an adjacent ligand. The largest and the second largest angles are measured between the centroids of the olefins (C35,C36-Ag3-C41,C42 and C20,C21-Ag3-C35,C36) with bond angles 127.4° and 119.0°, respectively. The calculated τ_4 value for Ag3 is 0.81, revealing a distorted trigonal pyramidal geometry. Ag2-N2 and Ag3-N7 have similar bond lengths (2.527 Å and 2.501 Å, respectively), which are longer than the Ag1-N3 bond length.

Ag4 is three coordinate through the coordination of two allyl arms from adjacent diallylamine groups of the same ligand and a nitrogen atom of the triazine ring. The largest bond angle is measured between the centroids of the coordinated olefins (C26,C27-Ag4-C38,C39) with a bond angle of 175.7°, which is very close to 180°. The other two bond angles are between the nitrogen atom of the triazine ring and the centroids of the olefins (N8-Ag4-C26,C27 and N8-Ag4-C38,C39) with bond angles 89.3° and 87.8°, respectively, which are very close to right angular. Considering these bond angles, Ag4 has T-shape geometry. Although the silver-carbon bond lengths are in the expected range for silver-olefin interactions, the bond length for

Ag4-N8 (2.630 Å), is longer than the usual silver-N-heterocyclic interaction. From the measured bond angles and bond lengths of silver with N-heterocyclic nitrogen atoms, the presence of high pyrimidalization of the triazine ring is obvious.

As shown in Figure 3.33B, Ag1 and Ag2 are bridged by the same ligand with a separation distance of 6.505 Å. Ag3 and Ag4 are bridged by the second ligand with a separation distance of 6.664 Å. Ag2 and Ag3 are bridged by the allyl arms from the same diallylamine group of the first ligand with a separation distance of 7.947 Å. The longest separation distance measured in this structure is Ag1····Ag4, with a separation distance of 13.276 Å.

With silver(I) triflate (**3.39**)

Ligand **3.36** was mixed with three equivalents of silver(I) triflate in acetone. Diethyl ether diffusion into the reaction mixture afforded crystals suitable for single crystal X-ray structure analysis. The structure was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains one full ligand molecule, three silver atoms, two coordinated and one non-coordinated triflate counter anions, revealing a 1:3 (ligand:metal) ratio or an M_3L_1 type coordination complex, as shown in Figure 3.34. The non-coordinated triflate counter anion is disordered over two sites with 57% dominant position occupancy.

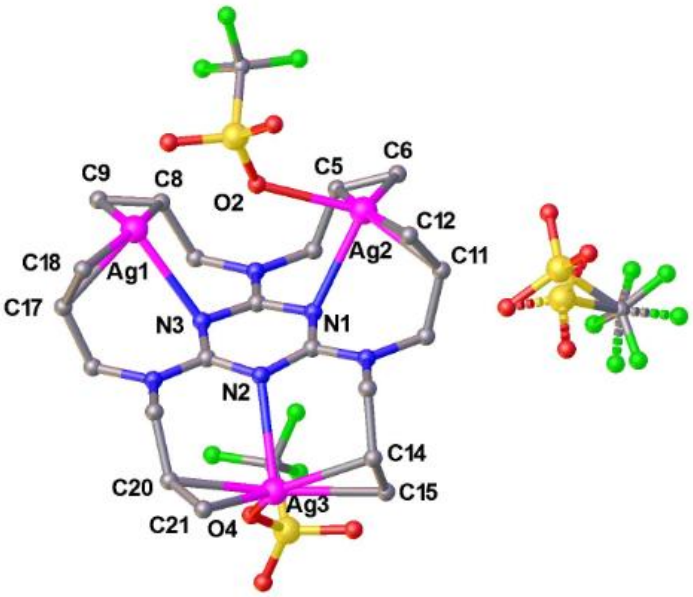


Figure 3.34 *– The trinuclear discrete assembly of complex* ***3.39****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°):Ag1-C8 2.427(4), Ag1-C9 2.379(4), Ag1-C8,C9 2.308(4), Ag1-C17 2.455(4), Ag1-C18 2.397(4), Ag1-C17,C18 2.334(4), Ag1-N3 2.485(3). N3-Ag1-C8,C9 92.7(2), N3-Ag1-C17,C18 90.8(2), C8,C9-Ag1-C17,C18 136.1(2). Ag2-C5 2.390(4), Ag2-C6 2.365(4), Ag2-C5,C6 2.281(4), Ag2-C11 2.421(4), Ag2-C12 2.347(4), Ag2-C11,C12 2.289(4), Ag2-N1 2.457(3), Ag2-O2 2.408(3), N1-Ag2-O2 80.2(2), N1-Ag2-C5,C6 95.5(2), N1-Ag2-C11,C12 91.2(2), O2-Ag2-C5,C6 100.8(2), O2-Ag2-C11,C12 118.3(2), C5,C6-Ag2-C11,C12 140.8(2). Ag3-O4 2.349(3), Ag3-N2 2.508(3), Ag3-C14 2.464(3), Ag3-C15 2.384(3), Ag3-C14,C15 2.331(3), Ag3-C20 2.429(3), Ag3-C21 2.405(4), Ag3-C20,C21 2.324(4), O4-Ag3-N2 94.5(1), O4-Ag3-C14,C15 116.7(2), O4-Ag3-C20,C21 112.2(2), N2-Ag3-C14,C15 89.7(2), N2-Ag3-C20,C21 90.7(2), C14,C15-Ag3-C20,C21 130.9(2).*

Once again, there are no two allyl arms from the same diallylamine group coordinated to a silver atom. The olefin groups C5=C6 and C8=C9 are from the same diallylamine group that coordinate with silver atoms in a “cis-mode” above the plane of the triazine ring. The other olefin groups from the same

diallylamine groups coordinate to silver in a “trans-mode”, as shown in Figure 3.34. Two of the nitrogen atoms (N1 and N3) coordinate above the plane of the triazine ring, while the other nitrogen atom (N2) coordinates to a silver below the plane of the triazine ring.

Ag1 is three coordinate through the coordination of two olefins (C8=C9 and C17=C18) and one nitrogen atom (N3). The largest angle is measured between the centroids of the olefins (C8,C9-Ag1-C17,C18) with a bond angle of 136.1°. The second and the third largest angles are between the nitrogen atom (N3) and the centroid of the two olefins (C8=C9 and C17=C18) with bond angles 92.7° and 90.8°, respectively. The silver-carbon bond distances are in the expected range for such interactions. The bond length for Ag1-N3 is 2.485 Å, which is longer than normal silver-N-heterocyclic interactions, but also shorter than some of the bond lengths measured in complexes **3.37** and **3.38**. From the measured bond angles, Ag1 has a distorted T-shape.

Ag2 is four coordinate through the coordination of two allyl arms from adjacent diallylamines (C5=C6 and C11=C12), one nitrogen atom (N1) from the triazine ring of the ligand and oxygen atom (O2) from the triflate counter anion. The Ag2-N1 bond length is 2.457 Å, which is similar to the bond length of Ag1-N3 (2.485 Å). The Ag2-O2 bond length is 2.408 Å, which is in the expected range for silver-oxygen interactions. The largest bond angle measured around the Ag2 environment is between the centroids of the two coordinated olefins (C5,C6-Ag2-C11,C12) with a bond angle of 140.8° and the second largest bond angle is measured between the oxygen atom (O2) of the triflate counter anion and the centroid of C11=C12 with a bond angle of 118.3°. The calculated τ_4 value for Ag2 is 0.72, which reveals a seesaw geometry.

Ag3 is also four coordinate through the coordination of the allyl arms from adjacent diallylamine groups (C14=C15 and C20=C21), a nitrogen atom (N2) from the triazine ring and oxygen atom (O4) from the triflate counter anion. The Ag3-N2 bond length is 2.508 Å, which is longer than the other two silver-nitrogen bond lengths measured in this structure. The Ag3-O4 bond length is 2.349 Å which is shorter than the Ag2-O2 bond length (2.408 Å). The largest

bond angle measured around the Ag3 environment is between the centroids of the two coordinated olefins (C14,C15-Ag3-C20,C21) with a bond angle of 130.9°. The second largest angle is measured between the triflate oxygen atom (O4) and the centroid of C14=C15 with a bond angle 116.7°. The calculated τ_4 value for Ag3 is 0.80, revealing a distorted trigonal pyramidal geometry.

An interesting feature of this structure is the coordination of all of the possible donating groups of the ligand with silver to produce a discrete assembly. The silver nitrogen distances are similar to each other and also shorter than some of the long interactions observed in complexes **3.37** and **3.38**. In general, all the silver atoms interact with two olefin groups and a nitrogen atom from the triazine ring, which makes ligand **3.36** a triply bridging ligand. Ag1-Ag2, Ag1-Ag3 and Ag2-Ag3 are all triply bridged by ligand **3.36** with separation distances of 4.913 Å, 6.529 Å and 6.477 Å, respectively.

3.5 Summary

This chapter has described the synthesis of seventeen ligands, of which four are new compounds. Depending on the number of diallylamine groups, these compounds are classified into three classes, as ligands containing one, two or three diallylamine groups. Other aromatic core structures like pyridine, pyrimidine and triazine rings are also deliberately incorporated into these compounds to induce silver(I) coordination with nitrogen atoms of the N-heterocyclic ring, which enables us to investigate the Ag-σ-donor coordination with nitrogen as well as Ag-π-donor coordination with the olefin group.

Most of the attempts to grow crystals of complexes containing benzene core structures were unsuccessful, except for ligand **3.12**. Despite the change in the core structure of the aromatic rings, ligands containing one diallylamine group (**3.12**–**3.16**) gave 1D polymeric assemblies. **3.17** is the only ligand with one diallylamine group that did not furnish crystalline complexes, despite numerous attempts with different silver(I) salts. Ligand **3.12** with silver(I) perchlorate gave a 1D polymeric assembly that involves the chelation of two allyl arms from the same diallylamine group, which is unique throughout this

project. Complexes of ligands **3.13–3.16** showed 1D polymeric assemblies, which do not have chelation of the allyl arms from the same diallylamine group; instead they chelate with the nitrogen atom of the N-heterocyclic ring.

Compounds containing two diallylamine groups, except for ligand **3.29** which contains a triazine core, failed to furnish crystals of complexes with different silver(I) salts. Ligand **3.29** gave discrete structures with silver(I) perchlorate and silver(I) triflate. Both structures are tetranuclear discrete assemblies, which involve the coordination of all four allyl arms, as well as the triazine core nitrogen atoms to form M_4L_2 type coordination complexes.

Ligands containing three diallylamine groups gave crystals of complexes with different silver(I) salts, except for ligand **3.34**. Ligand **3.35** with silver(I) triflate gave a discrete assembly that involves the coordination of the pyrimidine nitrogen atoms and the allyl arms closer to these nitrogen atoms with silver. Two allyl arms further from the pyrimidine nitrogen atoms of the core structure are not coordinated. The silver-nitrogen bond distances are longer than the literature values recorded for silver-N-heterocyclic nitrogen bond distances. Although this interaction is long and weak relative to other silver-N-heterocyclic interactions, it played a significant role in the assembly of the structure by coordination with silver that introduces pyrimidalization of the N-heterocyclic nitrogen atom, which keeps the two coordinated allyl arms in close proximity to silver. Ligand **3.36** formed a 1D polymeric assembly with silver(I) perchlorate that involves the coordination of five allyl arms out of six and two of the triazine nitrogen atoms with silver. **3.36** also formed a complex with silver(I) triflate but this time it is a discrete assembly that involves the coordination of all of the allyl arms as well as the triazine nitrogen atoms. The non-coordination of the two allyl arms observed in complex **3.35** is not observed here, which shows that the influence of the nitrogen atoms of the core structures affects the coordination of the allyl arms of the ligand.

In summary this chapter has described a total of fourteen new crystal structures; eleven of them are complexes, one new ligand and two salts of ligands **3.25** and **3.31**.

Chapter Four

Complexes of ligands containing allyl groups

Chapter Four

Complexes of ligands containing allyl groups

4.1 Introduction

One of the interesting features of metallosupramolecular chemistry is the use of ligand design to control the structure of the complex.[119] In order to achieve this, there are a number of factors to be considered like the flexibility of the ligand,[204-205] the separation distance between the binding sites,[206] the number and types of potential functional groups within the ligand.[26-27, 207-208] The use of non-aromatic linear core structures introduces flexibility within the ligand, while rigid core structures like aromatic rings reduces the flexibility of the ligand. The introduction of additional functional groups may assist in producing new and interesting assemblies, as well as evaluating the coordination potential of different functional groups towards a specific metal atom.[27]

The coordination of ligands containing olefin group with Cu(I) and Ag(I) salts has been studied by various researchers[125, 178, 209-210] for the sake of constructing different metallosupramolecular assemblies; however, in most of the studies the ligand molecules have other functional groups in addition to the olefin moiety. For instance, ligands **4.1**-**4.3**, shown in Figure 4.1, have carboxyl oxygen and pyridyl nitrogen atoms as possible coordination sites in addition to the olefin group. Depending on the types and number of functional groups involved in the coordination, these ligands with Cu(I) salts showed discrete dimeric, 1D and 2D polymeric assemblies.[210-215]

Under hydrothermal reaction conditions ligands **4.1**-**4.3** formed stable discrete dimeric assemblies with CuCl through the coordination of the olefinic functional group.[210-212] Neither the pyridine nitrogen nor the carboxyl oxygen atoms are coordinated with copper. Under solvothermal reaction conditions ligand molecule **4.2** reacted with $Cu(MeCN)_4(BF_4)$ to give a 1D polymeric assembly, through the coordination of the pyridyl nitrogen atom and the olefinic group, without the coordination of the carboxyl oxygen atoms.[210, 213]

Ligand **4.3** also gave a 1D polymeric coordination complex under the same conditions as ligand **4.2**.[210, 214] In both cases the ligand molecule bridges the copper atoms through the coordination of the pyridyl nitrogen and the alkene functional groups. 2D polymeric assemblies were achieved using ligands **4.1** and **4.2** with $Cu(MeCN)_4(BF_4)$ through the coordination of the two carboxylate oxygen atoms, the nitrogen atom of the pyridyl ring and the olefin moiety.[210, 212, 215]

In the above examples the copper atoms bridged by **4.1** and **4.2** through the coordination of all the possible donor groups of the ligand molecules. From the results observed above, the coordination of the carboxyl oxygen, the pyridyl nitrogen and the alkene to copper seems competitive; though the coordination of the olefin was observed with copper in all cases.

Reaction of ligand **4.4** under solvothermal reaction conditions with CuCl and CuBr formed 2D polymeric assemblies. The ligand bridges copper atoms through the coordination of the quinoline nitrogen and the alkene functional group.[210, 212, 216]

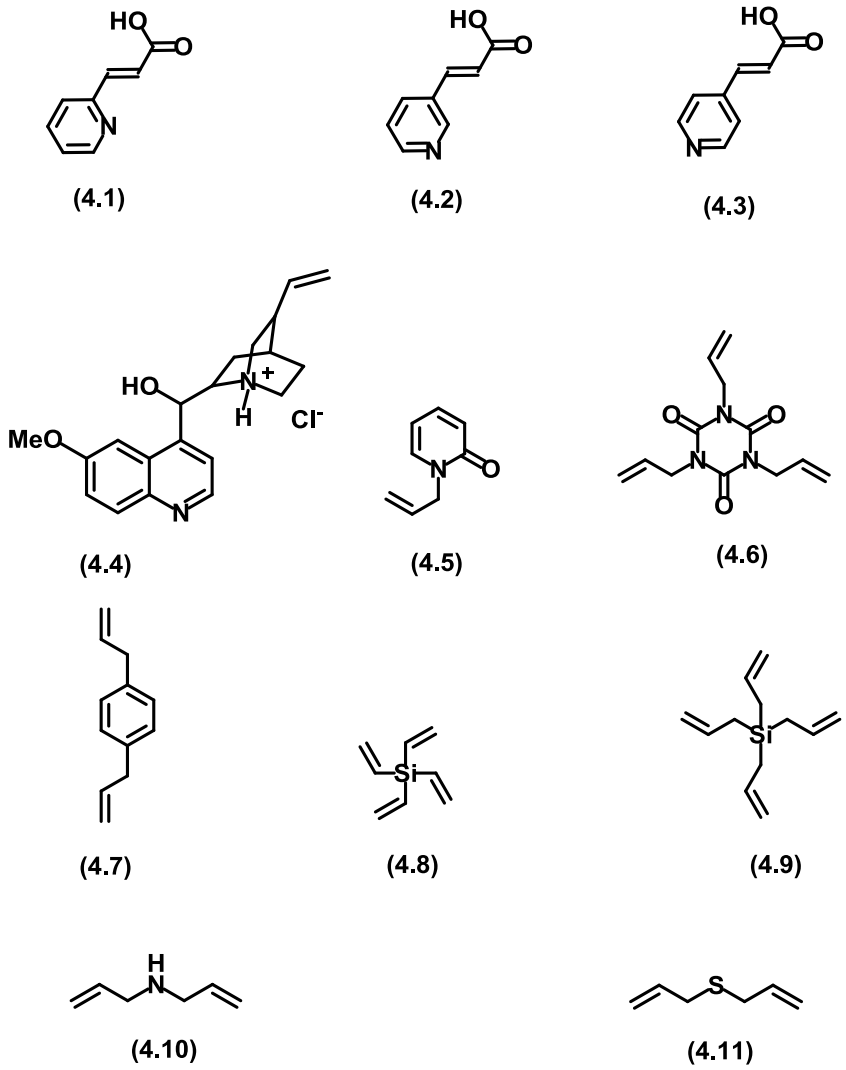


Figure 4.1 *– Examples of ligands previously used in the construction of different assemblies with copper(I) and/or silver(I).*

Ligand **4.6** contains carbonyl oxygen and olefin groups as possible donors. A copper cluster was obtained from the reaction of **4.6** with CuBr.[217] The copper clusters are bridged by the ligand molecule through the coordination of the alkene functional group. Recently, a complex of **4.6** with silver(I) was reported as a 1D polymeric assembly through the coordination of two of the three allyl arms.[56, 218] It is interesting to see ligand **4.5** formed three different M_2L_2 discrete assemblies with silver triflate, silver hexafluorophosphate and silver perchlorate through the coordination of the carbonyl oxygen and the allyl arm of the ligand,[60] while no coordination of the carbonyl oxygens of **4.6** was

observed with copper or silver.[217-218] The observation of these structures is one of the foundations for this project to further investigate the interaction of olefins with silver using urea based ligands, that contain both olefin functional groups and a carbonyl oxygen.

The use of ligands containing olefin group as metallosupramolecular synthons is not limited to the ligands that contain an olefin group attached to N-heterocyclic rings. Recently the Steel group described a 1D polymeric assembly using **4.7** with silver perchlorate;[56, 60] in which ligand **4.7** bridges two adjacent silver atoms through the allyl arms.

The coordination of ligands containing olefin with copper(I) or silver(I) was also observed in ligands with non-aromatic core structures. There are a few examples in the literature that showed ligand molecules with non-aromatic core structures could be used as metallosupramolecular synthons for the aforementioned metal atoms. For example, ligands **4.10** and **4.11** showed a chelating type coordination with silver(I) through the coordination of the olefin group of the allyl arms, while bridging to a second silver through the nitrogen and sulfur atoms respectively.[56, 219-220] Changing the core structure to silicon also showed interesting results by coordinating only through the olefin functional groups, as observed in the coordination of ligand **4.8** with copper(I)[221] and also in our previous work using ligand **4.9** and silver nitrate. [124]

The interaction of silver and ligands containing allyl arm with benzene core structures as metallosupramolecular synthons are well studied by previous Steel group members.[56, 60] This work was also extended using non-aromatic core structures like diallylether and triallylamine ligands. Here we extend this study further by using the ligands shown in Figure 2.

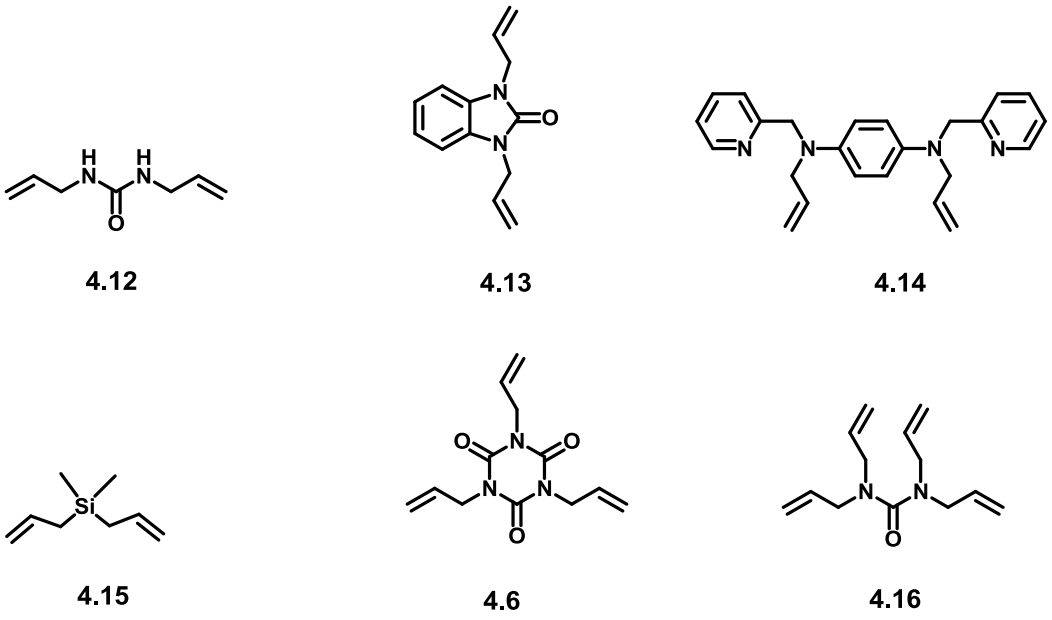
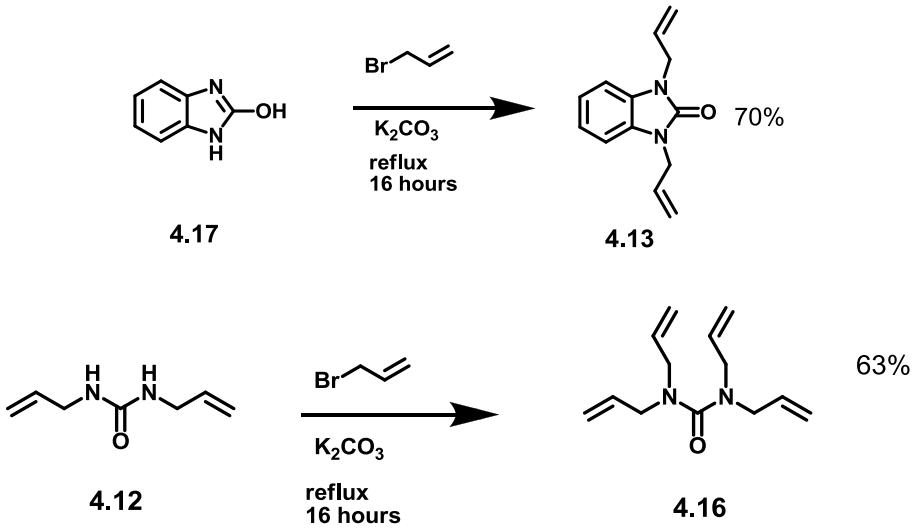


Figure 4.2 *– Ligand molecules used in this project.*

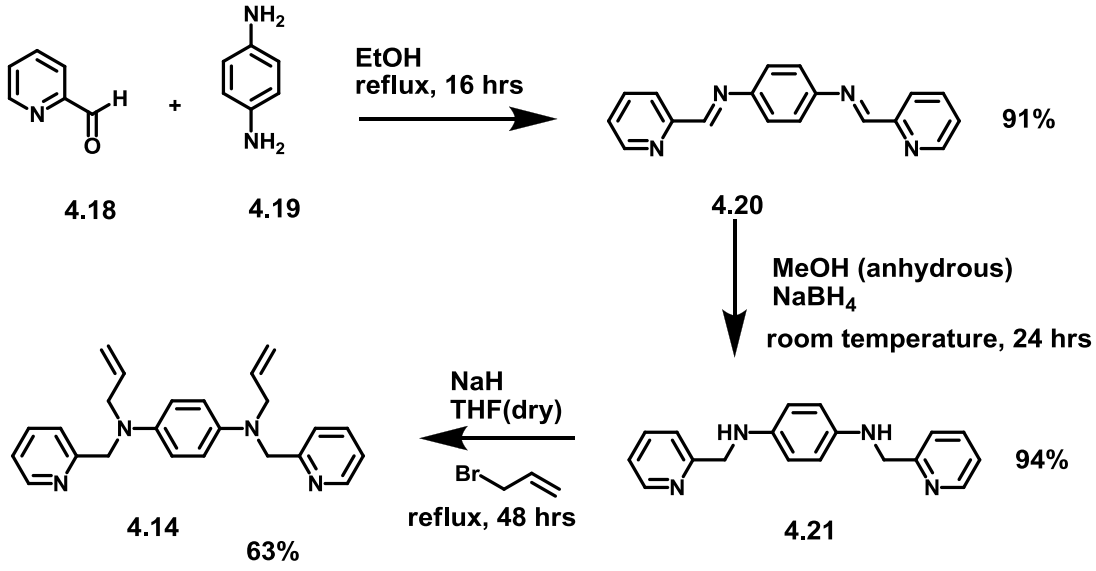
4.2 Ligand syntheses

Ligands **4.12**, **4.15** and **4.6** were commercially available. Ligands **4.13** and **4.16** were synthesised by the allylation of 2-hydroxybenzimidazole (**4.17**) and 1,3-diallylurea (**4.12**) using a literature method[142] under the conditions shown in the following scheme, in 70% and 63% yields, respectively.



Scheme 4.1 *– Reaction conditions for the synthesis of ligands* ***4.13*** *and* ***4.16****.*

Ligand **4.14** was synthesised from 2-pyridinecarboxaldehyde (**4.18**) and 1,4-diaminobenzene (**4.19**) in three steps using literature methods.[151, 222] The first step is coupling of **4.18** and **4.19**.[222] The synthetic procedure involves refluxing a solution of **4.18** and **4.19** in ethanol for 16 hours. Upon cooling the solution, yellow crystalline **4.20** was obtained in 91% yield. The second step of the synthesis, the reduction of the imine group in **4.20** to amine using sodium borohydride, resulting in the precursor **4.21** in 94% yield. The final step of the synthesis involves allylation of precursor **4.21** using the procedure[151] which has been used extensively in this project, as shown in scheme 4.2.



Scheme 4.2 *– Reaction conditions for the synthesis of ligand* ***4.14****.*

Ligand **4.14** was isolated as a brown oily liquid that grew crystals, upon standing, suitable for X-ray crystal structure analysis. The structure was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains half of the ligand molecule. The structure shows the two allyl arms of the ligand orienting themselves far apart from each other in a “trans” fashion, as shown in the following figure. The allyl arms are also oriented far from the pyridine nitrogen atoms.

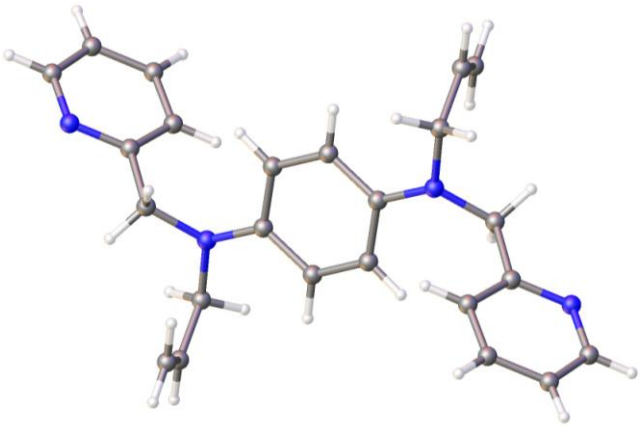


Figure 4.3 *– The X-ray structure of ligand* ***4.14****.*

*4.3 Complexes of 1,3-diallylurea (**4.12**)*

With silver(I) triflate (**4.22**)

A solution of 1,3-diallylurea *(***4.12***)* in acetone was mixed with an equimolar solution of silver(I) triflate in acetone. Slow diffusion of diethyl ether into the reaction mixture resulted in the growth of crystals suitable for X-ray crystallography. The structure was solved in the triclinic P-1 space group. The asymmetric unit contains one full ligand, one silver atom and a coordinated triflate counter anion revealing a 1:1 (metal:ligand) ratio or an M_1L_1 type complex. One of the allyl arms and the oxygen atom of the carbonyl functional group of the ligand coordinated with silver, while the other allyl arm is non-coordinated, as shown in Figure 4.4. The non-coordinated allyl arm is disordered over two sites with dominant position occupancy of 60%.

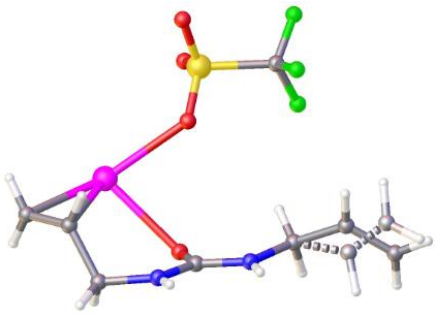
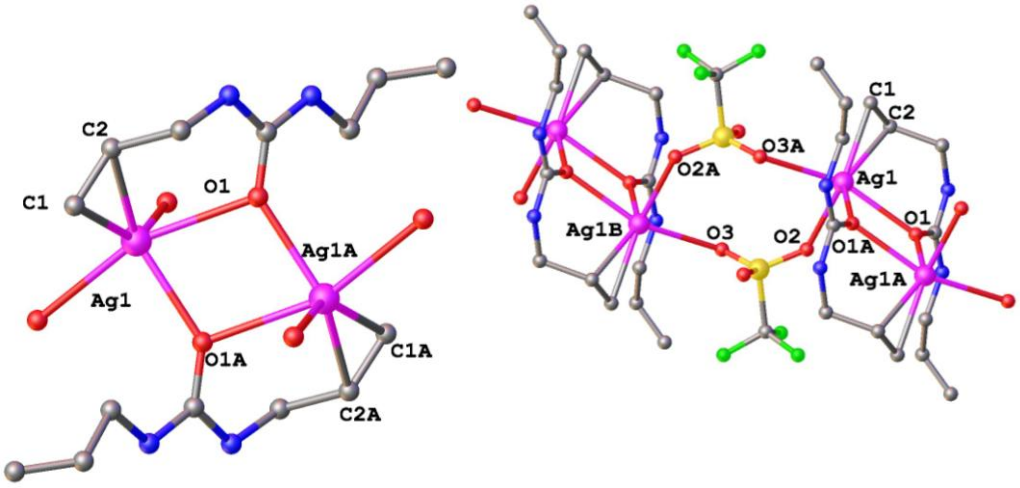


Figure 4.4 *- The asymmetric unit of complex* ***4.22*** *showing the coordination of one of the allyl arms, the carbonyl oxygen of the ligand and an oxygen atom of the triflate counter anion. The*

non-coordinated disordered allyl arm is shown in a light broken bond.

The ligand coordinates to silver through the alkene functional group of one of the allyl arms and the carbonyl oxygen atom. The carbonyl oxygen atom coordinated with two silver atoms, while the alkene functional group coordinated with only one silver atom, as shown in Figure 4.5A. The ligand molecule bridges two neighbouring silver atoms through the coordination of the carbonyl oxygen (Ag1A-O1-Ag1). The carbonyl oxygen and the alkene functional group of the allyl arm are chelated to a silver atom (Ag1). Therefore, the ligand molecule acts as both a bridging and chelating type ligand. Interestingly, the triflate counter anion bridges two tetragonal shaped assemblies by coordinating with two neighbouring silver atoms, as shown in Figure 4.5B.



A) *B)*

***Figure 4.5** – A) Part of the polymeric structure of complex **4.22** showing the tetragonal assembly due to the coordination of O1 with Ag1 and Ag1A. B) Part of the polymeric structure of complex **4.22** showing the bridging of two tetragonal assemblies by the triflate counter anions.*

The structure grows into a 1D polymeric structure by bridging the tetragonal shaped assembly through the triflate counter anion. Silver has a coordination number of 5 by coordinating with four different oxygen atoms

and one alkene functional group with a calculated τ_5 value of 0.435, revealing a distorted square pyramidal shape. The Ag1-Ag1A distance (3.768 Å) is shorter than the distance Ag1-Ag1B (5.770 Å). One of the tetragonal sides (Ag1-O1 (2.495 Å)) is slightly longer than the other (Ag1-O1A (2.315 Å)) side. The angle O1-Ag1-O1A 76.9^o is narrower than that of Ag1-O1-Ag1A 103.1^o. A quadrilateral structure, which has opposite sides and angles equal to one another but is neither equilateral nor right angled can be classified as a parallelogram or a rhomboid. Therefore, the tetragonal shaped structure can be called a rhomboid-like structure. The structure can be classified as a 1D polymeric rhomboid assembly bridged by a triflate counter anions.

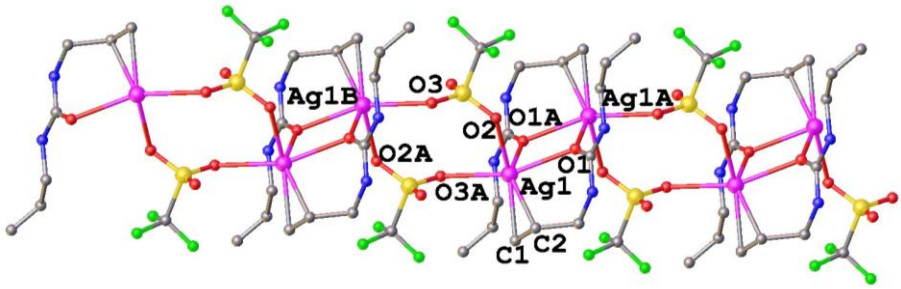


Figure 4.6 *– 1D polymeric structure of complex* ***4.22****. All hydrogen atoms and the disorder have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O1 2.495(1), Ag1-O1A 2.315(1), Ag1-O2 2.411(1), Ag1-O3A 2.586(1), Ag1-C1 2.351(2), Ag1-C2 2.430(2), Ag1-C1,C2 2.295(2), O1-Ag1-O1A 76.9(4), Ag1-O1-Ag1A 103.1(4), O1-Ag1-O2 78.6(4), O1-Ag1-O3A 158.0(4), O1-Ag1-C1 105.1(2), O1-Ag1-C2 81.3(2), O1-Ag1-C1,C2 93.1(2), O2-Ag1-O1A 94.9(4), O2-Ag1-O3A 92.1(4), O2-Ag1-C1 142.0(2), O2-Ag1-C2 116.1(2), O2-Ag1-C1,C2 129.5(2), O1A-Ag1-C1 122.9(2), O1A-Ag1-C2 137.5(2), O1A-Ag1-C1,C2 131.9(2), O3A-Ag1-C1 94.5(2), O3A-Ag1-C2 120.6(2), O3A-Ag1-C1,C2 108.0(2).*

All the oxygen-silver bond distances are less than the sum of the ionic radii between silver(I) and oxygen. The Ag1-O3A bond distance (2.586 Å) is

longer than the other silver(I)-oxygen bond distances. The non-coordinated oxygen and the fluorine atoms of the counter anion are oriented in opposite directions. This orientation minimizes the steric clash with the non-coordinated allyl arm. Although the orientation of the counter anion towards the non-coordinated allyl arm minimizes the probability of hydrogen bonding between the fluorine atoms and the hydrogen atoms of the allyl arm, it keeps the non-coordinated oxygen atom of the triflate anion in a very close proximity with the hydrogen atom of the NH group of the non-coordinated allyl arm from the next layer of the polymer, as shown in Figure 4.7. Hydrogen bonding between layers give the structure more stability and transforms the structure from a 1D to 2D type polymer. The growth of a polymer structure into another dimension through hydrogen bonding is common in the literature.[10, 223]

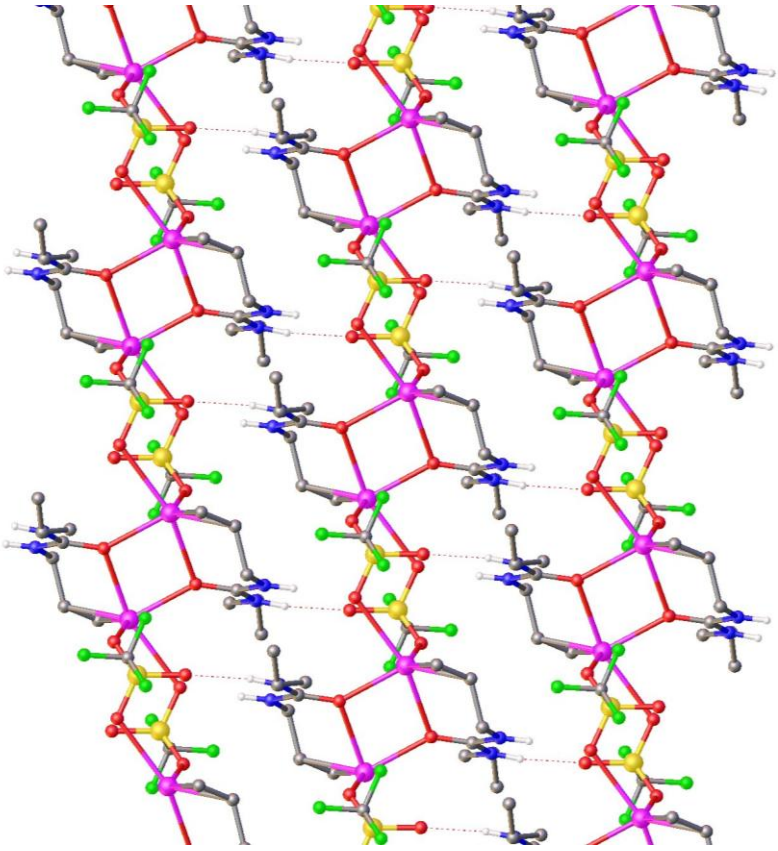


Figure 4.7 *– Part of the 2D polymeric assembly of complex* ***4.22*** *due to the hydrogen bonding between layers of 1D polymeric*

sheets. The disorder and all the hydrogen atoms except the NH have been omitted for clarity.

The non-coordinated oxygen atom of the triflate counter anion has an interlayer hydrogen bonding interaction with the hydrogen atom of the NH group of the non-coordinated allyl arm of the ligand with bond distances (Å) and angles (°), as shown in table 4.1.

D-H⋯⋯A	D-H	H⋯⋯A	D⋯⋯A	D-H⋯⋯A
N-H⋯⋯O	0.880	2.062	2.898	158.344

Table 4.1 *Hydrogen bonding geometry with the triflate counter anion.*

The hydrogen bonding observed in this structure is stronger than the reported hydrogen bonding of N-H⋯Cl and N-H⋯O in literature[197-198] but weaker than the "head-to-head" N-H⋯⋯O hydrogen bonding observed in the work of Stang *et al.*[224]

<u>With silver(I) tetrafluoroborate (**4.23**)</u>

Diethyl ether diffusion into a mixture of silver(I) tetrafluoroborate and 1,3-diallylurea in acetone, followed by slow evaporation, grows crystals suitable for X-ray crystal structure analysis. The structure was solved in the monoclinic $P2_1/c$ space group. The asymmetric unit contains four full ligand molecules, four silver(I) atoms and four non-coordinated tetrafluoroborate counter anions within two crystallographically independent units, as shown in the following Figure. One of the tetrafluoroborate anions has a disorder over two positions with 56% dominant position occupancy.

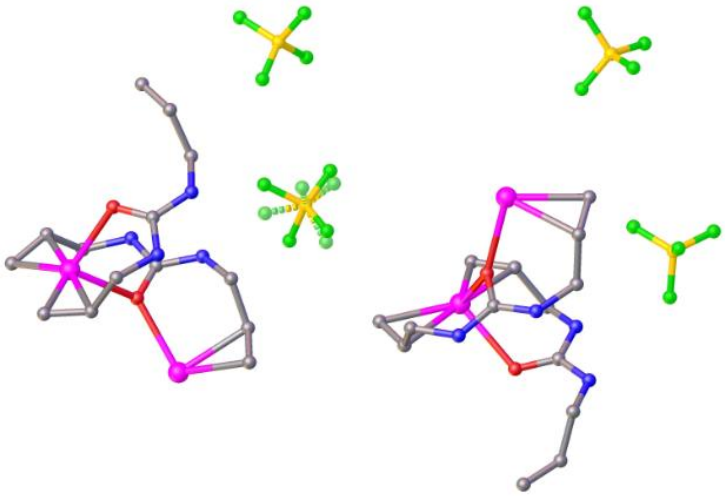
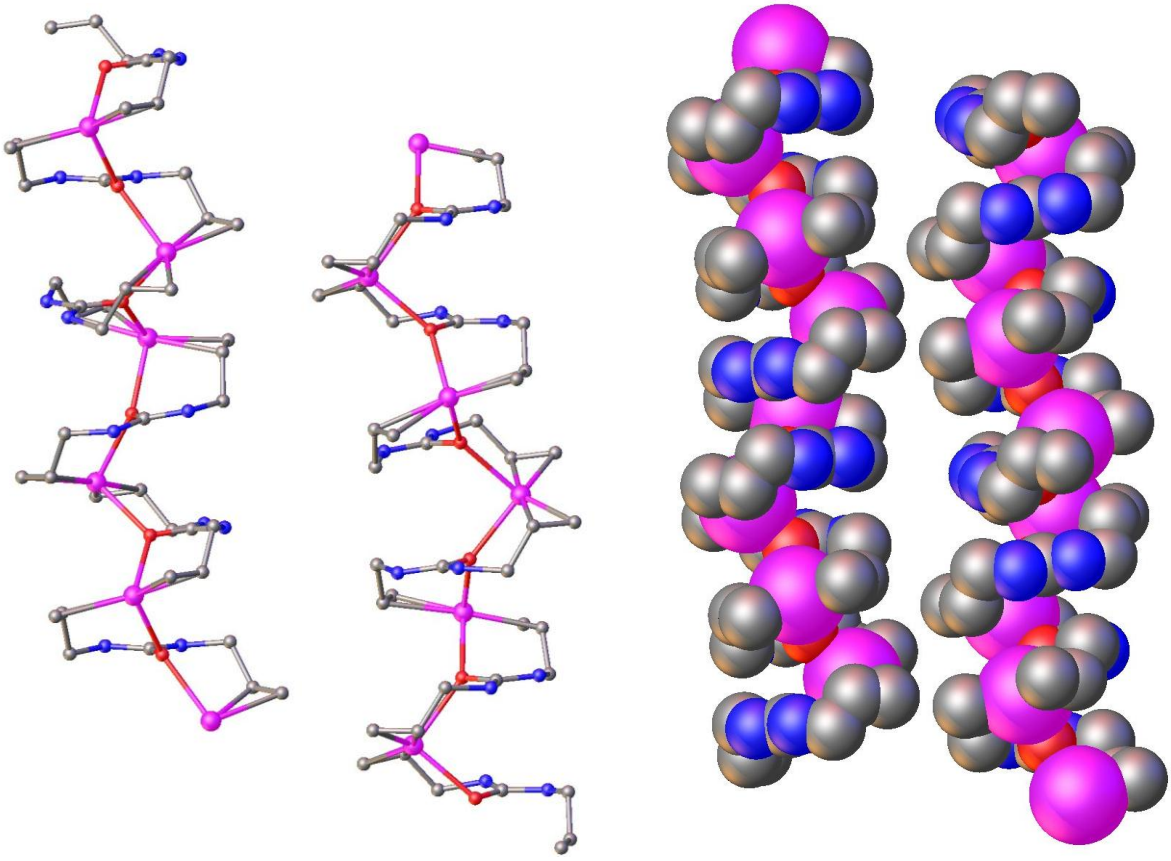


Figure 4.8 *- The asymmetric unit of complex* ***4.23****. All hydrogen atoms have been omitted for clarity. The disorder in one of the tetrafluoroborate anion is shown with broken bonds.*

Both allyl arms of the ligand are coordinated with silver through the olefinic functional groups, while in complex **4.22** the ligand coordinated through only one of the allyl arms. The carbonyl oxygen coordinates with two silver atoms as observed in complex **4.22**. The interaction of both allyl arms of the ligand and the absence of any interaction from the counter anion leads **4.23** to have a different structure from **4.22**. The structure grows into a 1D helical structure, as shown in the following Figure.



A) B)

Figure 4.9 *– A) The helical structure of* ***4.23*** *in a ball and stick diagram B) Space filling diagram of the helical structure of* ***4.23****. All hydrogen atoms and the counter anions have been omitted for clarity.*

The ligand molecule again acts in both a chelating and bridging manner, as observed in complex **4.22**. Both the carbonyl oxygen and the alkene functional groups of the ligand are coordinated with two different silver atoms. The ligand is acting in a tetradentate manner. The silver atoms are bridged by both the allyl arm and the carbonyl oxygen atom. Since the carbonyl atom and the allyl arm of the same ligand molecule are coordinating with the same silver atom, the ligand also acts in a chelating fashion, as shown in Figure 4.10. Having a very flexible structure with the carbonyl functional group equidistant from the allyl arms makes this ligand a very good candidate for a helical assembly.[36, 119]

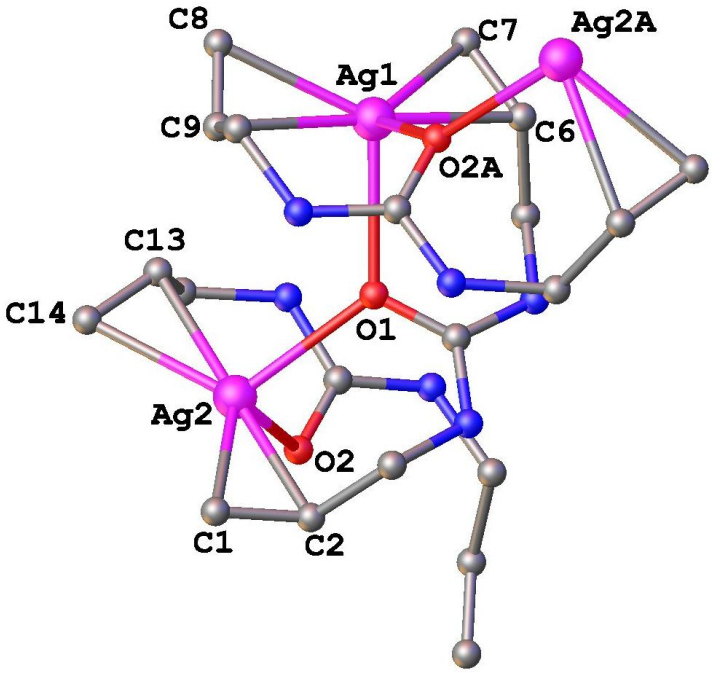


Figure 4.10 *– Part of the 1D helical structure showing both chelating and bridging coordination of the ligand with silver. All hydrogen atoms and tetrafluoroborate counter anions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O1 2.425(2), Ag1-O2A 2.400(2), Ag1-C6 2.363(3), Ag1-C7 2.357(3), Ag1-C6,C7 2.261(3), Ag1-C8 2.374(3), Ag1-C9 2.390(3), Ag1-C8,C9 2.285(3), O1-Ag1-O2A 93.0(2), O1-Ag1-C6 85.3(2), O1-Ag1-C7 108.1(1), O1-Ag1-C6,C7 96.8(2), O1-Ag1-C8 116.9(2), O1-Ag1-C9 92.2(2), O1-Ag1-C8,C9 104.8(2), O2A-Ag1-C6 100.5(2), O2A-Ag1-C7 121.8(2), O2A-Ag1-C6,C7 111.7(2), O2A-Ag1-C8 102.9(2), O2A-Ag1-C9 83.5(2), O2A-Ag1-C8,C9 93.2(2), C6-Ag1-C8 146.4(1), C6-Ag1-C9 175.4(1), C7-Ag1-C8 113.1(1), C7-Ag1-C9 145.4(1), C6,C7-Ag1-C8,C9 146(1), Ag2-O1 2.412(2), Ag2-C1 2.343(3), Ag2-C2 2.356(3), Ag2-C1,C2 2.250(3), Ag2-O2 2.406(2), Ag2-C13 2.375(3), Ag2-C14 2.350(3), Ag2-C13,C14 2.266(3), O1-Ag2-C1 107.1(2), O1-Ag2-C2 85.5(2), O1-Ag2-C1,C2 96.4(2), O1-Ag2-O2 95.9(2), O1-Ag2-C13 93.7(2), O1-Ag2-C14 118.5(2), O1-Ag2-C13,C14 106.4(2), C1-Ag2-O2 119.7(2), C2-Ag2-O2 98.1(2), C1,C2-Ag2-*

O2 92.9(2), C1-Ag2-C13 145.6(1), C1-Ag2-C14 113.2(1), C2-Ag2-C13 177.9(1), C2-Ag2-C14 146.5(1), C1,C2-Ag2-C13,C14 146.3(1), O2-Ag2-C13 83.9(2), O2-Ag2-C14 101.9(2), O2-Ag2-C13,C14 92.9(2)

The silver is four coordinate with two alkene functional groups of the allyl arms, and two oxygen atoms of the carbonyl group of the ligand. The largest angles around the silver atoms (Ag1 and Ag2) are between the centroids of the alkene functional groups and the smallest angles are between O2 and the alkene functional groups. C6,C7-Ag1-C8,C9 (146.0°) and C1,C2-Ag2-C13,C14 (146.3°) are the largest angles. O2-Ag2-C13,C14 (92.9°) and O2-Ag1-C8,C9 (93.2°) are the smallest angles. The calculated τ_4 values for Ag1 and Ag2 are 0.73 and 0.74 respectively, indicating a seesaw-type geometry. The distance Ag1-O1 (2.425 Å) is longer than the distance Ag1-O2A (2.400 Å). The distance Ag2-O1 (2.412 Å) is longer than the distance Ag2-O2 (2.406 Å). The silver atoms are doubly bridged by the ligand molecule with the same separation distance of 4.458 Å. The distance between Ag1-Ag1A (7.933 Å) is longer than the distance between Ag2-Ag2A (7.837 Å).

*4.4 Complexes of 1,3-diallylbenzimidazol-2-one (**4.13**)*

With silver (I) perchlorate (**4.24**)

Ligand **4.13**, in acetone, was mixed with an equimolar amount of silver(I) perchlorate solution in acetone. Diethyl ether diffusion into the solution resulted in the growth of crystals suitable for X-ray crystal analysis. The structure was solved in the triclinic P-1 space group. The asymmetric unit contains one full ligand, one silver atom and one coordinated perchlorate anion revealing a 1:1 (metal:ligand) or M_1L_1 type complex, as shown in Figure 4.11. The overall structure of the complex is a 1D ladder type polymeric structure that involves the coordination of the two allyl arms through the alkene functional groups and the carbonyl oxygen of the ligand.

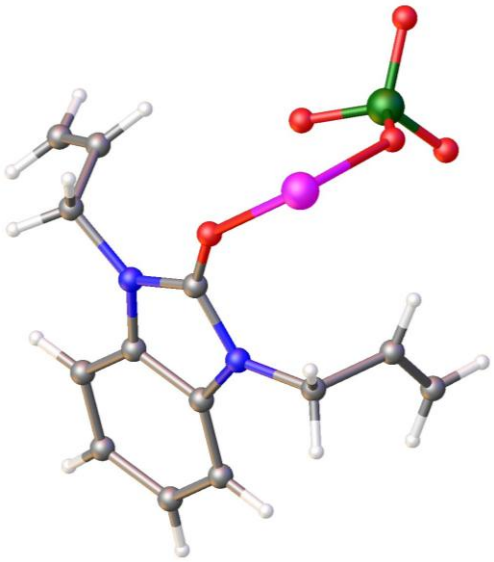


Figure 4.11 *– The asymmetric unit of complex* ***4.24***

The silver atom is four coordinate with two alkene functional groups of the allyl arms, an oxygen atom of the carbonyl group of the ligand and an oxygen atom of the perchlorate counter anion. The smallest angle is O1-Ag1-O4 (85.0°) and the two largest bond angles are O1-Ag1-C12,C13 (137.2°) and C9,C10-Ag1-C12,C13 (124.5°), as shown in Figure 4.12. The calculated τ_4 value for silver is 0.70, indicating a seesaw shape. The bond distance of the coordinated carbonyl oxygen atom of the ligand (O1-Ag1, 2.278 Å) is much shorter than the coordinated perchlorate oxygen (O4-Ag1, 2.529 Å). The bond distances between the coordinated carbon atoms of the alkene functional group of the ligand and the silver atom are in the expected bond distance range for the olefin carbon-silver interaction. The distance from the centre of C9=C10 to silver (2.406 Å) is longer than the distance from the centre of C12=C13 to silver (2.324 Å).

The ligand acts in a tridentate manner, bridging three different silver atoms, each with different separation distances. The separation distance between Ag1-Ag1A (5.498 Å) is shorter than the separation distance between Ag1-Ag1B (7.089 Å) while the separation distance between Ag1A-Ag1B (10.790 Å) is the longest.

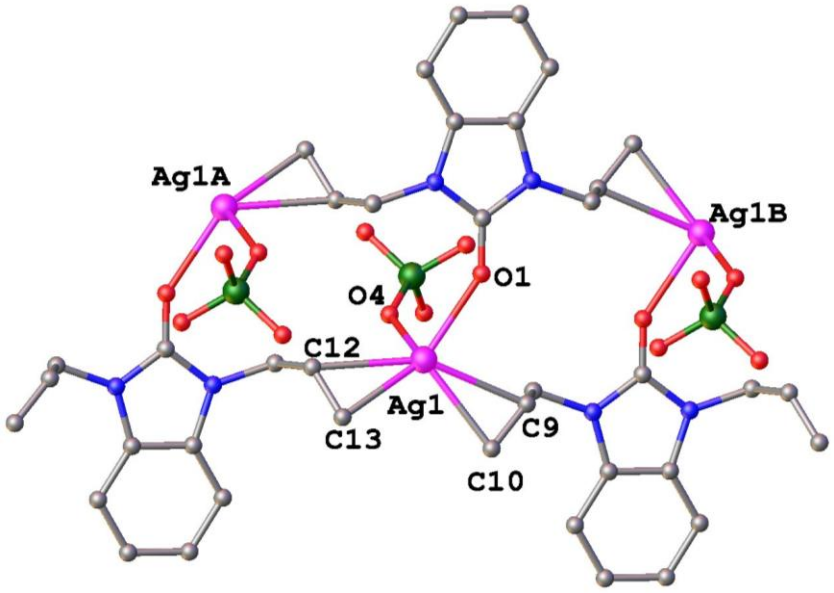
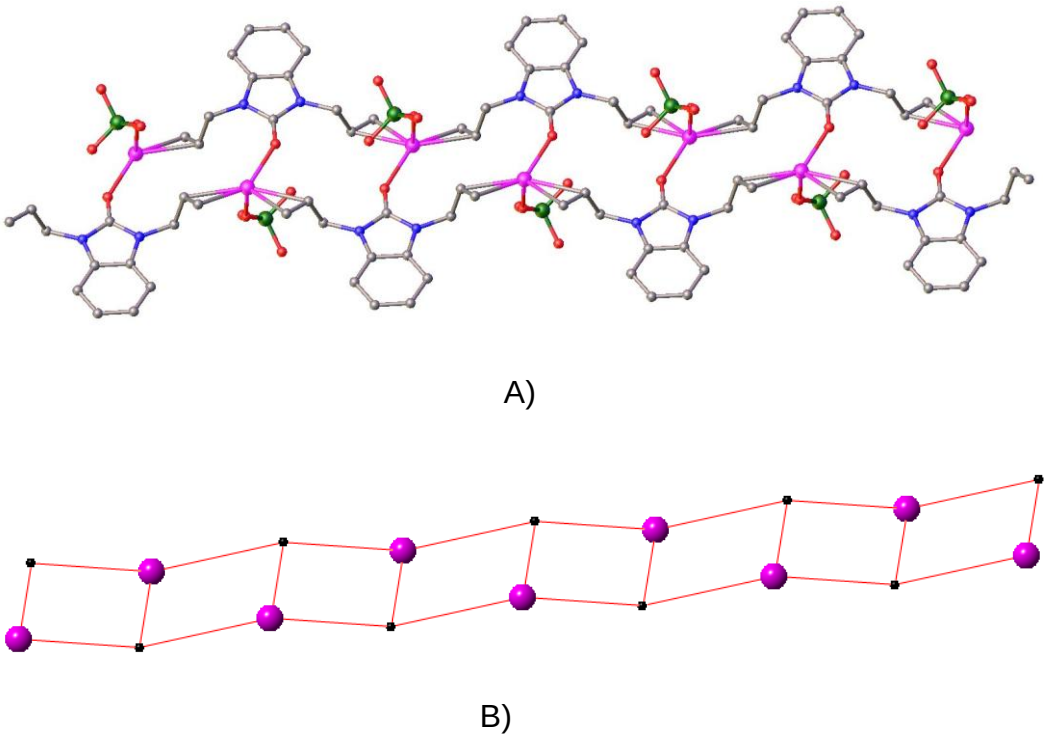


Figure 4.12 *– Part of the 1D ladder polymeric structure of complex* ***4.24****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O1 2.278(2), Ag1-O4 2.529(2), Ag1-C9 2.538(2), Ag1-C10 2.456(2), Ag1-C9,C10 2.406(2), Ag1-C12 2.491(2), Ag1-C13 2.343(2), Ag1-C12,C13 2.324(2), O1-Ag1-O4 85.0(1), O1-Ag1-C9 81.0(1), O1-Ag1-C10 108.9(1), O1-Ag1-C9,C10 94.7(1), O1-Ag1-C12 125.7(1), O1-Ag1-C13 146.6(2), O1-Ag1-C12,C13 137.2(2), O4-Ag1-C9 100.9(2), O4-Ag1-C10 115.8(2), O4-Ag1-C9,C10 108.8 (2), O4-Ag1-C12 84.7(1), O4-Ag1-C13 108.1(2), O4-Ag1-C12,C13 96.2(2), C9-Ag1-C12 153.3(2), C9-Ag1-C13 124.1(2), C10-Ag1-C12 123.5(2), C10-Ag1-C13 93.1(2), C9,C10-Ag1-C12,C13 124.5(2).*

The allyl arms of the ligand are coordinated with two different silver atoms (Ag1A and Ag1B), which build the sides of a ladder, while the carbonyl oxygen of the ligand coordinates with a third silver atom (Ag1-O1) which provides the rungs of the ladder structure. The ligand is positioned coplanar to the plane of the other side of another ligand with an undulating arrangement that minimizes the steric clash between them, as shown in Figure 4.13. The perchlorate anions are arranged above and below the coordination plane alternatively, which minimizes the steric clash between them.



A)

B)

Figure 4.13 *– A) Part of the 1D ladder polymeric structure of* ***4.24****, all hydrogen atoms have been omitted for clarity. B) Schematic presentation of the ladder structure of the complex (pink balls represent silver and the black dots represent the ligand molecule).*

With silver(I) triflate (**4.25**)

A solution of silver(I) triflate in acetone was mixed with an equimolar solution of ligand **4.13** in acetone. Diethyl ether diffusion into the mixture resulted in the growth of crystals suitable for X-ray crystal structure analysis. The structure was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand, one silver atom coordinated with one of the allyl arms of the ligand through the alkene functional group, a coordinated water molecule and a non-coordinated triflate counter anion revealing a 1:1 (metal:ligand) ratio or M_1L_1 complex, as shown in Figure 4.14. The two allyl arms are positioned above and below the plane of the aromatic core structure of the ligand. The overall structure of the complex is a 1D polymeric assembly that involves the coordination of both allyl arms through the alkene functional group of the ligand without the involvement of the carbonyl oxygen atom.

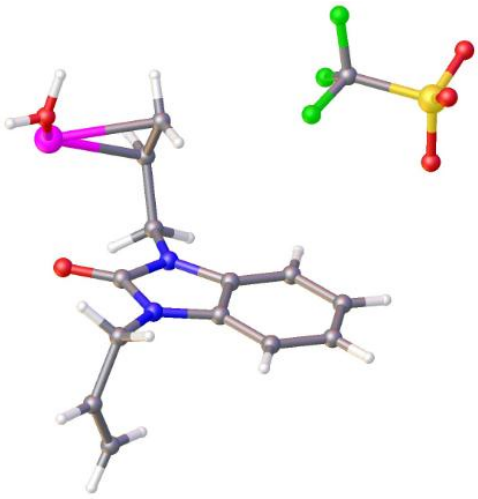


Figure 4.14 *– The asymmetric unit of complex* ***4.25****, showing the arrangement of the allyl arms above and below the aromatic core of the ligand. All hydrogen atoms except for the water have been omitted for clarity.*

Unlike complex **4.24**, the silver is three coordinate with two allyl arms through their alkene functional group and a water molecule. The carbonyl oxygen atom and the triflate counter anion are non-coordinated. The ligand acts as a bidentate bridging ligand that bridges two neighbouring silver atoms through the coordination of the allyl arms. The separation distance between the two neighbouring silver atoms (Ag1-Ag1A) is 5.544 Å. Unlike the coplanar arrangement observed in complex **4.24**, the ligand molecule in **4.25** is positioned perpendicular to the plane of the other ligand; however, the ligand alternates its position similarly to **4.24** minimizing the steric hindrance between the ligand molecules, as shown in Figure 4.15. The arrangement of the ligand in such a perpendicular and alternating assembly avoids any possibility of π-π interactions between the aromatic rings of the ligand. All the bond distances between silver and the olefinic carbons are in the expected range. The oxygen-silver bond distance (Ag1-O2, 2.252 Å) from the water molecule is relatively short. The largest bond angle around silver atom is observed between the centroids of the two alkene functional groups (C8,C9-Ag1-C12,C13, 134.4°). The bond angle between the oxygen atom of the water molecule and the centroids of the two alkene functional groups are almost the same with O2-Ag1-C8,C9, 113.6° and O2-Ag1-C12,C13, 111.9°. From the

observed bond angles we can conclude that the silver atom has a distorted trigonal geometry.

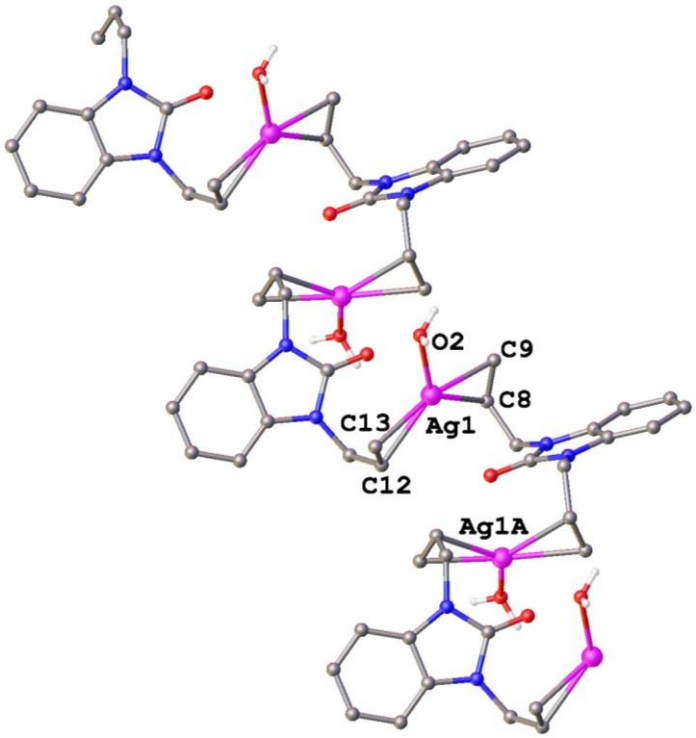


Figure 4.15 *– Part of the 1D polymeric assembly of complex* ***4.25****. The triflate counter anion and all the hydrogen atoms except for the water molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O2 2.252(3), Ag1-C8 2.431(3), Ag1-C9 2.344(4), Ag1-C8,C9 2.291(4), Ag1-C12 2.437(3), Ag1-C13 2.354(3), Ag1-C12,C13 2.300(3), C12-Ag1-O2 126.8(2), C12-Ag1-C8 103.0(2), C12-Ag1-C9 135.6(2), C13-Ag1-O2 96.2(2), C13-Ag1-C8 134.0(2), C13-Ag1-C9 166.1(2), C8,C9-Ag1-C12,C13 134.4(2), O2-Ag1-C8 129.7(2), O2-Ag1-C9 97.0(2), O2-Ag1-C8,C9 113.6(2), O2-Ag1-C12,C13 111.9(2).*

The water molecule in **4.25** assembled up and down alternatively minimizing the steric hindrance. Two of the oxygen atoms of the triflate counter anion hydrogen bond with the water molecule, as shown in Figure 4.16.

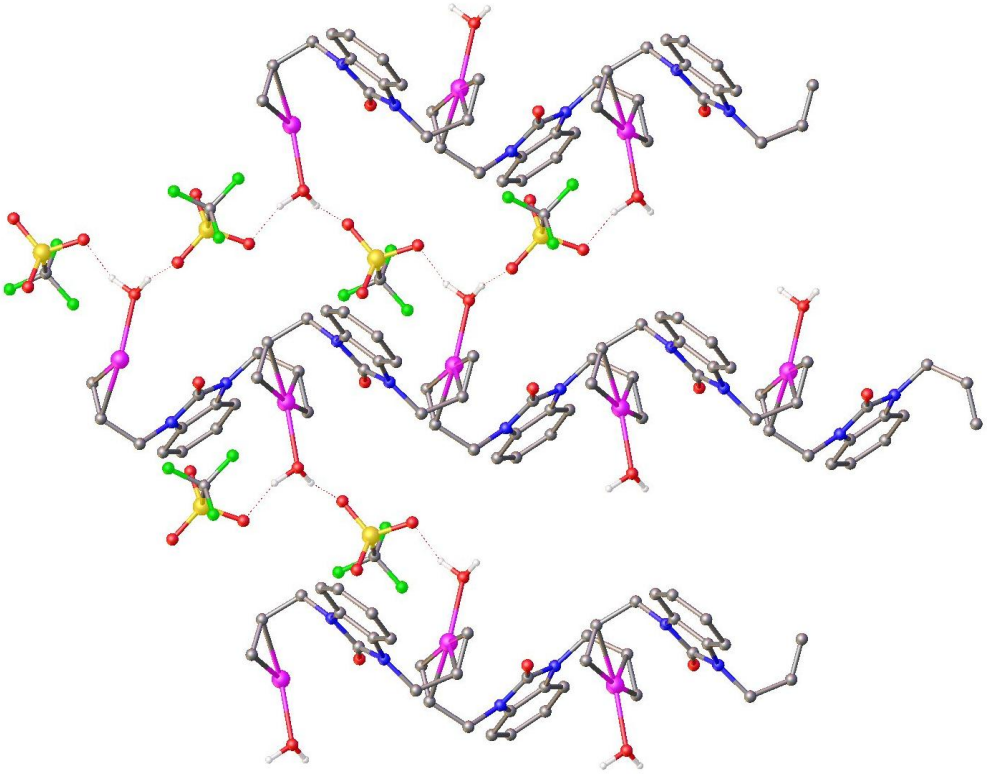


Figure 4.16 *– The interlayer hydrogen bonding between the triflate counter anion and the coordinated water molecule in complex* ***4.25****. All the hydrogen atoms except for the water molecules have been omitted for clarity.*

Even though there is interlayer hydrogen bonding between the coordinated water molecule and the triflate counter anion, the structure is still a 1D polymeric assembly.

D-H····A	D-H	H····A	D····A	D-H····A
O-H····O	0.827	1.908	2.706	162.01
O-H····O	0.947	1.808	2.722	161.19

Table 4.2 *Hydrogen bonding geometry with the triflate counter anion.*

The interlayer hydrogen bonding observed in **4.25** is shorter and stronger than some of the hydrogen bonding (O-H···O) observed in the literature.[10, 225]

With silver(I) tetrafluoroborate (**4.26**)

A solution of silver(I) tetrafluoroborate in acetone was mixed with an equimolar solution of ligand **4.13** in acetone. Diethyl ether diffusion followed by slow evaporation of the solvent over a period of time resulted in the growth of crystals suitable for single crystal X-ray analysis. The structure was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand, one silver atom and one non-coordinated tetrafluoroborate counter anion, as shown in Figure 4.17. The tetrafluoroborate anion has disorder over two positions, with 84% dominant position occupancy.

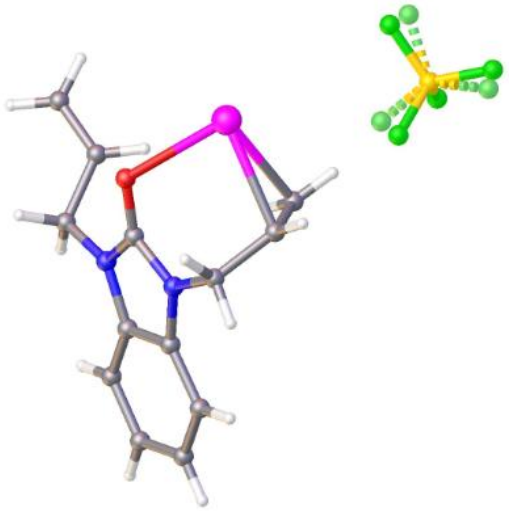


Figure 4.17 *– The structure of the asymmetric unit of complex* ***4.26*** *showing the coordination of one of the allyl arms and the carbonyl oxygen of the ligand and the non-coordinated tetrafluoroborate with its disorder.*

The overall structure of the complex is a discrete binuclear assembly that involves the coordination of both allyl arms and the carbonyl oxygen atom of the ligand, as shown in Figure 4.18. The silver atom is four coordinate with two allyl arms and two carbonyl oxygen atoms from adjacent ligands. The largest bond angle in the structure is 139.5° between O1A and the centroid of C9A,C10A (O1A-Ag1-C9A,C10A) followed by 124.7° between the centroid of

the two allyl arms (C9A,C10A-Ag1-C12,C13) of the ligand. The calculated τ_4 value for silver is 0.68 indicating a seesaw shape. The observed silver-carbon bond distances are in the expected range for this type of interaction. The bond distance for Ag1-O1 (2.554 Å) is longer than the bond distance for Ag1-O1A (2.305 Å) but both are in the typical bonding range for a silver-oxygen interaction.

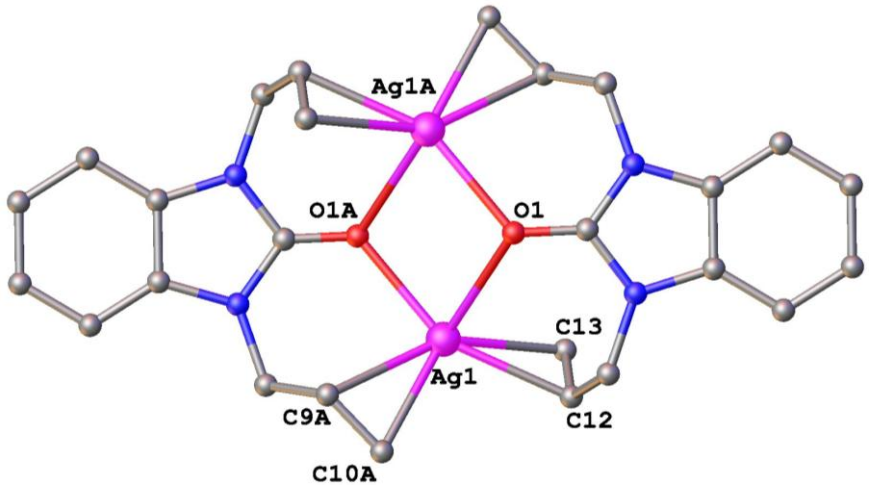


Figure 4.18 *– The binuclear discrete assembly of complex* ***4.26****. All hydrogen atoms and the tetrafluoroborate counter anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C12 2.395(2), Ag1-C13 2.393(2), Ag1-C12,C13 2.297(2), Ag1-O1 2.554(2), Ag1-C9A 2.434(2), Ag1-C10A 2.412(2), Ag1-C9A,C10A 2.327(2), Ag1-O1A 2.305(1), C12-Ag1-O1 83.5(1), C13-Ag1-O1 84.6(1), C12,C13-Ag1-O1 83.8(1), C12-Ag1-C9A 126.7(2), C12-Ag1-C10A 94.9(2), C13-Ag1-C9A 152.6(2), C13-Ag1-C10A 121.5(2), C12,C13-Ag1-C9A,C10A 124.7(2), C12-Ag1-O1A 152.9(2), C13-Ag1-O1A 124.6(2), C12,C13-Ag1-O1A 139.5(2), O1-Ag1-C9A 115.6(2), O1-Ag1-C10A 123.5(2), O1-Ag1-C9A,C10A 120.8(2), O1-Ag1-O1A 78.1(4), C9A-Ag1-O1A 79.7(1), C10A-Ag1-O1A 111.8(1), C9A,C10A-Ag1-O1A 95.6(1).*

Both ligand molecules are coplanar facing their coordination sites towards each other. The allyl arms orient on opposite sides of the aromatic plane,

which is suitable for the formation of the discrete assembly. The ligand acts as a tetradentate molecule by coordinating through the allyl arms and the carbonyl oxygen atom. Both the allyl arms and the carbonyl oxygen bridge Ag1-Ag1A with a separation distance of 3.776 Å. The formation of a tetragonal structure between the carbonyl oxygen atoms and the silver, with two different bond distances (2.554 Å and 2.305 Å), is similar to that observed in complex **4.22**. If we consider the coordination of one allyl arm and the carbonyl oxygen from the same ligand with silver atom, the ligand acts in a chelating mode. Therefore the ligand acts in a chelating and a bridging manner similar to that observed in complex **4.22**.

With silver(I) hexafluorophospahate (**4.27**)

A solution of silver(I) hexafluorophosphate in acetone was mixed with an equimolar solution of ligand (**4.13**) in acetone. Slow diffusion of diethyl ether into the reaction mixture followed by slow evaporation of the solvent resulted in the growth of crystals suitable for single crystal structure analysis. The structure was solved in the triclinic P-1 space group. The asymmetric unit contains one full ligand coordinated through one of the allyl arms and carbonyl oxygen, one silver atom, one coordinated water molecule and one non-coordinated hexafluorophosphate counter anion revealing a 1:1 (ligand:metal) complex or an M_1L_1 type coordination complex, as shown in Figure 4.19.

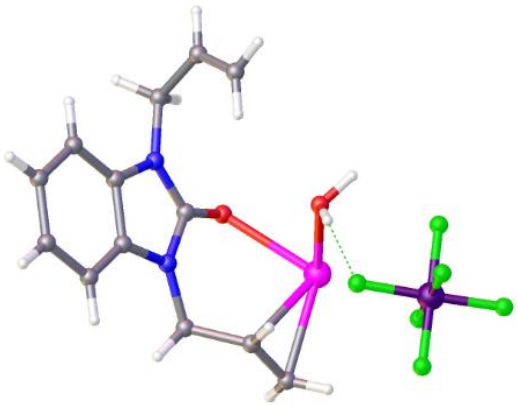


Figure 4.19 – The asymmetric unit of complex **4.27**. All hydrogen atoms have been omitted for clarity.

The overall structure of the complex is a binuclear discrete assembly that involves the coordination of both allyl arms of the ligand through the alkene functional group, the carbonyl oxygen atom and a water molecule, as shown in Figure 4.20. The silver atom is four coordinate with an oxygen atom from the carbonyl functional group of the ligand, a water molecule and two alkene functional groups from two different ligands. The largest bond angle observed between the centroid of the coordinated alkene functional groups (C8A,C9A-Ag1-C12,C13) is 130.5°. The second largest bond angle observed between the carbonyl oxygen atom of the ligand molecule (O1) and the centroid of one of the coordinated allyl arms (C8A=C9A) is 125.8°. The calculated τ_4 value for silver is 0.74, indicating a seesaw shape.

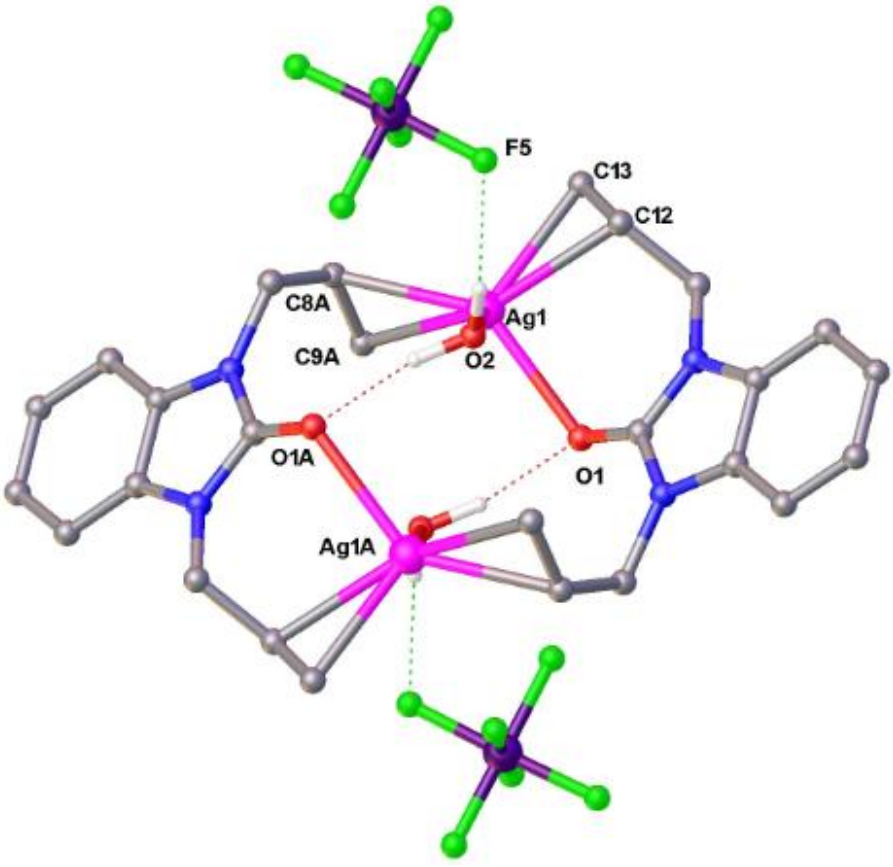


Figure 4.20 *– The binuclear discrete assembly of complex* ***4.27****. All hydrogen atoms except for the water molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-O1 2.419(3), Ag1-O2 2.422(3), Ag1-C12 2.473(4), Ag1-C13 2.433(4), Ag1-C12,C13 2.359(4), Ag1-C8A 2.458(4), Ag1-C9A*

2.381(4), Ag1-C8A,C9A 2.326(4), O1-Ag1-O2 78.9(2), O1-Ag1-C12 85.0(1), O1-Ag1-C13 107.1(1), O1-Ag1-C12,C13 96.1(1), O1-Ag1-C8A 139.3(1), O1-Ag1-C9A 111.1(1), O1-Ag1-C8A,C9A 125.8(1), O2-Ag1-C12 86.3(1), O2-Ag1-C13 112.5(1), O2-Ag1-C12,C13 99.4(1), O2-Ag1-C8A 103.9(1), O2-Ag1-C9A 119.5(1), O2-Ag1-C8A,C9A 112.3(1), C12-Ag1-C8A 135.4(1), C12-Ag1-C9A 151.1(1), C13-Ag1-C8A 108.8(1), C13-Ag1-C9A 119.5(1), C12,C13-Ag1-C8A,C9A 130.5(1).

Ligand **4.13** again acts in both bridging and chelating modes. The coordination of the alkene functional group of **4.13** with silver bridges neighbouring silver atoms (Ag1-Ag1A) with a separation distance of 4.699 Å. Unlike complex **4.27**, the carbonyl oxygen atom of the ligand is coordinated with only one silver atom. The coordination of the carbonyl oxygen atom and the olefin functional group of the same ligand with the same silver atom makes **4.13** a chelating ligand. All the silver-carbon bond distances are in the expected range for silver olefinic carbon bond distances. The Ag1-O1 bond distance (2.419 Å) is more or less the same as the Ag1-O2 bond distance (2.422 Å). Unlike the orientation of the allyl arms observed in complex **4.27**, the orientation of the allyl arms of the ligand are on the same side of the aromatic plane. The two ligands are not in a “head-on” coplanar arrangement; instead one is a little bit above the plane of the other ligand molecule that fits with the formation of the discrete assembly. This orientation also gives the right space for the water molecule to coordinate with silver. The water molecules are coordinated in opposite directions minimizing any steric interaction; moreover, the water molecule has hydrogen bonding interactions with the carbonyl oxygen atom of the ligand and a fluorine atom of the hexafluorophosphate counter anion.

D-H·····A	D-H	H·····A	D····A	D-H····A
O-H·····O	0.950	1.833	2.767	167.256
O-H·····F	0.929	2.055	2.934	157.049

Table 4.3 *Hydrogen bonding geometry of the water molecule with the carbonyl oxygen atom of the ligand and the hexafluorophosphate counter anion.*

*4.5 Complexes of N^1,N^4-diallyl-N^1,N^4-bis(2-pyridinylmethyl)benzene-1,4-diamine (**4.14**)*

A number of attempts were made to grow crystals suitable for single crystal structure analysis by combining a solution of ligand **4.14** with different ratios and types of silver salts, but these were not successful.

*4.6 Complexes of diallyldimethylsilane (**4.15**)*

With silver(I) triflate (**4.28**)

An equimolar amount of diallyldimethylsilane (**4.15**) was mixed with a solution of silver(I) triflate in acetone. Diethyl ether diffusion followed by slow evaporation of the solvent resulted in the growth of block-like crystals suitable for single crystal structure analysis. The structure solved in the triclinic P-1 space group. The asymmetric unit of the complex contains one full ligand molecule, one silver atom and one coordinated triflate counter anion revealing a 1:1 (metal:ligand) ratio or an M_1L_1 type coordination complex, as shown in Figure 4.21. The ligand acts in a bridging fashion by coordinating with two neighbouring silver atoms (Ag1-Ag1B) with a separation distance of 9.068 Å. The structure grows into a 1D ladder type polymeric assembly through the coordination of the allyl arms of **4.15**, which act as the sides of the ladder.

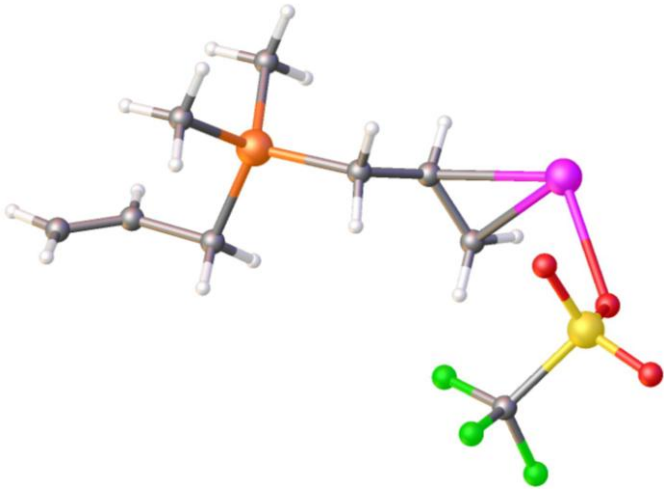


Figure 4.21 *– The asymmetric unit of complex* ***4.28*** *showing the coordination of one of the allyl arms through the alkene functional group and the coordinated triflate counter anion.*

The triflate counter anion coordinates with two silver atoms forming a tetragonal structure between the coordinated oxygen and silver atoms, as shown in Figure 4.22. The triflate counter anion bridges two neighbouring silver atoms (Ag1-Ag1A) with a separation distance of 3.908 Å. The bond distance between Ag1-O1A (2.459 Å) is longer than the bond distance between Ag1-O1 (2.435 Å). The bond angle O1A-Ag1-O1 is 74.0° and the bond angle Ag1-O1-Ag1A is 106.0°. This tetragonal structure is similar to complex **4.22**, and acts as the rungs of the ladder. The triflate counter anions coordinate with silver from opposite directions, one is above and the other is below the plane of the silver atoms, which minimizes the steric clash between them. The silver atom is four coordinate with two alkene functional groups of two different ligand molecules and two oxygen atoms from different triflate counter anions. The largest bond angle is between the centroid of the two coordinating alkene functional groups (C7A,C8A-Ag1-C1,C2) 129.5° and the second largest angle is between O1A and the centroid of (C7A=C8A) 115.0°. Four of the six bond angles around silver are close to 109.5° with calculated τ_4 value of 0.82, which reveals a trigonal pyramidal shape.

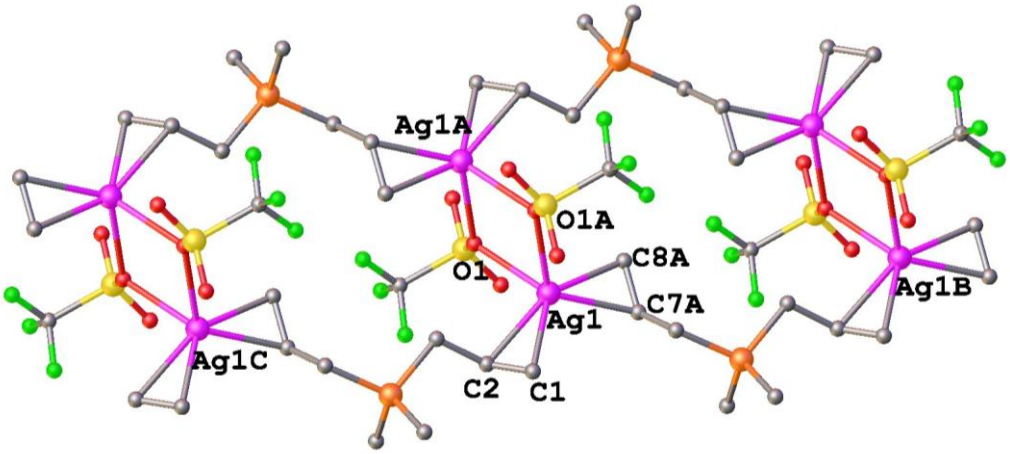


Figure 4.22 *– Part of the 1D ladder structure of complex* ***4.28****. All the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C7A 2.457(3), Ag1-C8A 2.378(3), Ag1-C7A,C8A 2.324(3), Ag1-O1 2.459(2), Ag1-C1 2.351(4), Ag1-C2 2.445(4), Ag1-C1,C2 2.315(4), Ag1-O1A 2.433(2), C7A-Ag1-O1 119.4(2), C8A-Ag1-O1 96.7(1), C7A,C8A-Ag1-O1 108.6(1), C7A-Ag1-C1 102.4(1), C7A-Ag1-C2 123.8(1), C8A-Ag1-C1 134.0(2), C8A-Ag1-C2 153.8(2), C7A,C8A-Ag1-C1,C2 129.5(1), C7A-Ag1-O1A 127.3(1), C8A-Ag1-O1A 101.5(1), C7A,C8A-Ag1-O1A 115.0(1), O1-Ag1-C1 110.0(2), O1-Ag1-C2 108.8(1), O1-Ag1-C1,C2 110.1(2), O1-Ag1-O1A 74.0(2), C1-Ag1-O1A 121.2(1), C2-Ag1-O1A 91.2(1), C1,C2-Ag1-O1A 105.9(1).*

All the silver-carbon bond distances are in the expected range for such interactions. Since the separation distances for Ag1-Ag1B and Ag1-Ag1C are equal (9.068 Å), the ladder structure is straight. Due to the same bond distances between the silver atoms on the side of the ladder structure, the undulation of the ladder structure observed in complex **4.24** is not observed in this structure, as shown in Figure 4.23.

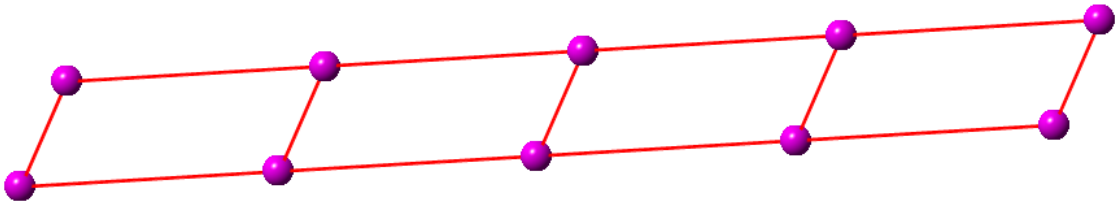


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Figure 4.23 *– The topology diagram for the 1D ladder structure. (The pink balls represent silver atoms)*

*4.7 Complexes of triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (**4.6**)*

With silver(I) hexafluorophosphate (**4.29**)

One equivalent of **4.6** was mixed with three equivalents of silver(I) hexafluorophosphate in acetone. Diethyl ether diffusion into the reaction mixture resulted in the growth of crystals suitable for single crystal structure analysis. The structure was solved in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand, one silver atom, a coordinated water molecule and a non-coordinated hexafluorophosphate counter anion, revealing a 1:1 (metal:ligand) or M_1L_1 type complex, as shown in Figure 4.24.

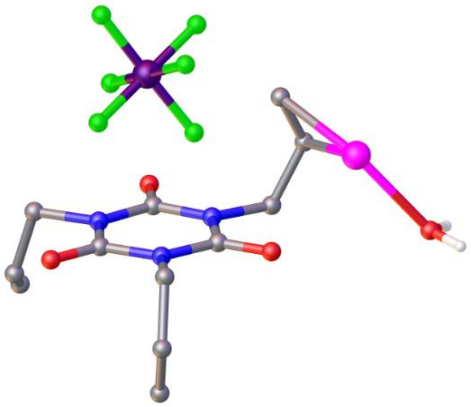


Figure 4.24 *– The asymmetric unit of complex **4.29**. Except for the water molecule all hydrogen atoms have been omitted for clarity.*

The coordinated allyl arm is positioned above the plane of the triazine ring, while the other two allyl arms are below the plane of the triazine ring, as shown in Figure 4.24. The structure grows into a 1D zigzag polymeric

assembly involving coordination of two of the allyl arms. The silver atom is three coordinate involving the coordination of two allyl arms from two different ligand molecules and a water molecule, as shown in Figure 4.25.

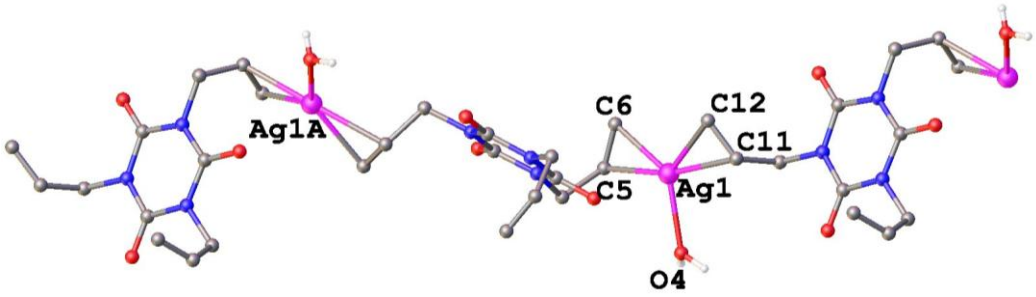


Figure 4.25 *– Part of the 1D polymeric assembly of complex* ***4.29****. The hexafluorophospahte counter anion and all hydrogen atoms (except for the water molecule) have been omitted for clarity. Selected bond lengths (Å) and angles(°): Ag1-C5 2.430(4), Ag1-C6 2.392(3), Ag1-C5,C6 2.319(4), Ag1-O4 2.276(3), Ag1-C11 2.398(3), Ag1-C12 2.348(3), Ag1-C11,C12 2.278(3), C5-Ag1-O4 95.5(1), C6-Ag1-O4 127.0(1), C5,C6-Ag1-O4 111.1(1), C5-Ag1-C11 165.5(1), C6-Ag1-C11 134.5(1), C5-Ag1-C12 136.0(1), C6-Ag1-C12 104.4(1), C5,C6-Ag1-C11,C12 135.9(1), O4-Ag1-C11 96.9(1), O4-Ag1-C12 128.5(1), O4-Ag1-C11,C12 112.6(1).*

The largest bond angle around the silver is formed between the centroid of the two alkene functional groups of the allyl arms (C5,C6-Ag1-C11,C12) 135.9°. The other two bond angles are formed between O4 and the centroid of the coordinated alkene functional groups, (O4-Ag1-C11,C12) 112.6° and (O4-Ag1-C5,C6) 111.1°. From the measured bond angles the silver has a distorted trigonal geometry. The ligand acts in a bridging fashion with a separation distance (Ag1-Ag1A) of 10.204 Å. One of the allyl arms and the three oxygen atoms in the triazine ring are not coordinated. The allyl arms are coordinated with silver in a “trans-coordination mode” as observed in the coordination of **4.6** with Cu_4Br_4 cubane clusters[217], and also with silver(I) tetrafluoroborate.[218] One of the carbonyl oxygen atoms of the ligand molecule and the hexafluorophosphate counter anion are involved in an intermolecular

hydrogen bond with the coordinated water molecule. Even though there is interlayer hydrogen bonding, the overall topology of the polymer is still a 1D zigzag polymeric assembly, as shown in Figure 4.26.

The F····H distance observed in this structure is shorter than the F···H distance observed in **4.6** with silver(I) tetrafluoroborate[218] and also the F····H bond distance observed in other work.[226]

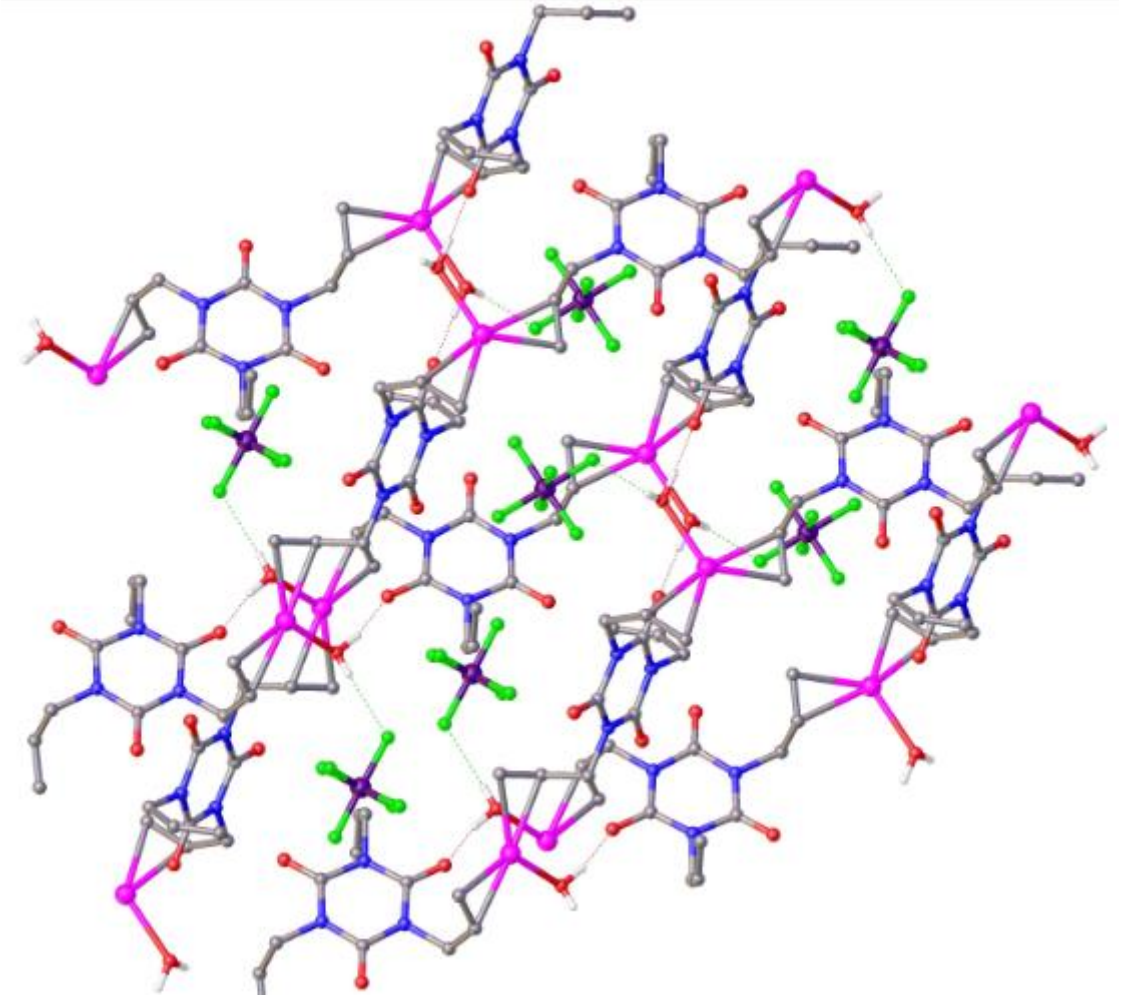


Figure 4.26 *– Part of the polymeric structure of complex* ***4.29*** *showing the interchain hydrogen bonding between the coordinated water molecule, one of the carbonyl oxygen atoms of the ligand and the hexafluorophosphate counter anion.*

D-H····A	D-H	H····A	D····A	D-H····A
O-H····O	0.885	1.873	2.737	164.96
O-H····F	0.702	2.144	2.814	159.82

Table 4.4 *Hydrogen bonding geometry from the water molecule to the oxygen atom of one of the carbonyl groups of the ligand and the hexafluorophosphate counter anion.*

With silver(I) nitrate (**4.30**)

One equivalent of ligand **4.6** was mixed with three equivalents of silver(I) nitrate solution in water. Slow evaporation of the solvent resulted in the growth of crystals suitable for X-ray structural analysis. The X-ray crystal structure is similar to complex **4.29** and crystallises in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one full ligand, one silver atom and one nitrate counter anion, as shown in Figure 4.27.

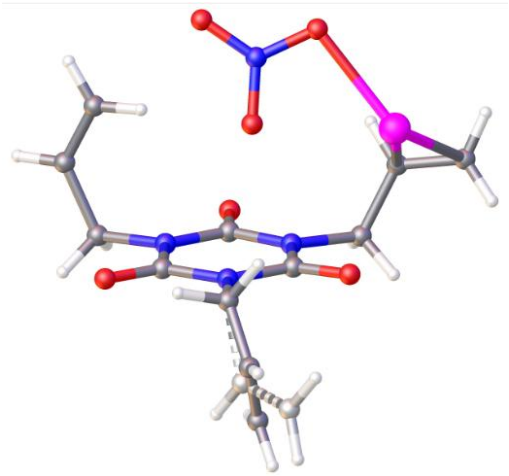


Figure 4.27 *– The asymmetric unit of complex* ***4.30****. The disordered allyl arm is shown with broken bonds.*

As shown in Figure 4.27, one of the allyl arms is disordered over two positions with 57% dominant position occupancy. The structure grows into a 1D polymeric assembly through the coordination of two allyl arms from two different ligand molecules and a nitrate anion, as shown in Figure 4.28. The

nitrate anion is coordinated with silver in a monodentate manner. The largest bond angle around silver is 132.1°, which is formed between the centroid of the two alkene functional groups (C8,C9-Ag1-C11A,C12A). The second and third largest bond angles around the silver atom are formed between the oxygen atom of the nitrate anion and the centroid of the alkene functional groups (O5-Ag1-C8,C9 114.2° and O5-Ag1-C11A,C12A 110.6°).

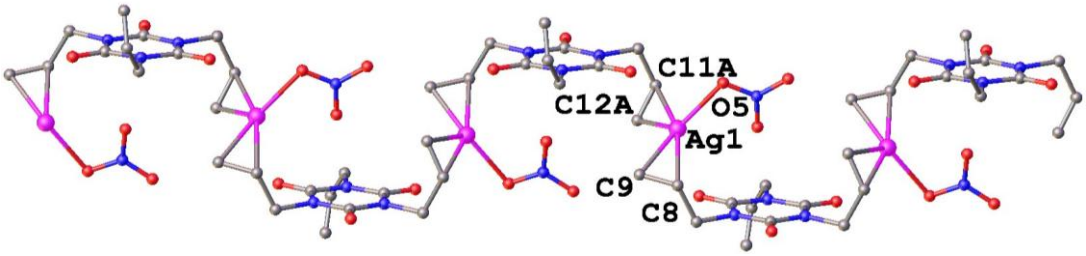


Figure 4.28 *– Part of the 1D polymeric assembly of complex* ***4.30****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C8 2.498(3), Ag1-C9 2.418(4), Ag1-C8,C9 2.365(4), Ag1-O5 2.347(3), Ag1-C11A 2.467(3), Ag1-C12A 2.384(3), Ag1-C11A,C12A 2.333(3), C8-Ag1-O5 104.7(2), C9-Ag1-O5 122.8(2), C8,C9-Ag1-O5 114.2(2), C8-Ag1-C11A 159.6(2), C8-Ag1-C12A 128.5(2), C9-Ag1-C11A 130.5(2), C9-Ag1-C12A 104.4(2), C8,C9-Ag1-C11A,C12A 132.1(2), O5-Ag1-C11A 95.0(2), O5-Ag1-C12A 126.7(2), O5-Ag1-C11A,C12A 132.1(2).*

The two allyl arms coordinated to silver are oriented in the same direction as the plane of the triazine ring in a “cis-coordination mode”, which is contrary to the observation in complex **4.29** which has a “trans-coordination mode”. The “cis-coordination mode” observed in the coordination of **4.6** with Cu_6Br_6 prismane clusters involves the coordination of all three allyl arms with the cluster;[217] and also in our earlier work with silver(I) perchlorate, as shown in Figure 4.29.[124] It is worth mentioning that in all of the coordination complexes of ligand **4.6** with different Ag(I) salts as well as the Cu(I) clusters, except in the complex with silver(I) perchlorate, the carbonyl oxygen atoms are not coordinated with the metal centres. In the complex of **4.6** with silver(I)

perchlorate, one of the carbonyl oxygen atoms of the ligand from the trione functionality is coordinated with the silver atom. This silver atom is the only four coordinate metal atom from these complexes; the rest are three coordinate silver atoms.

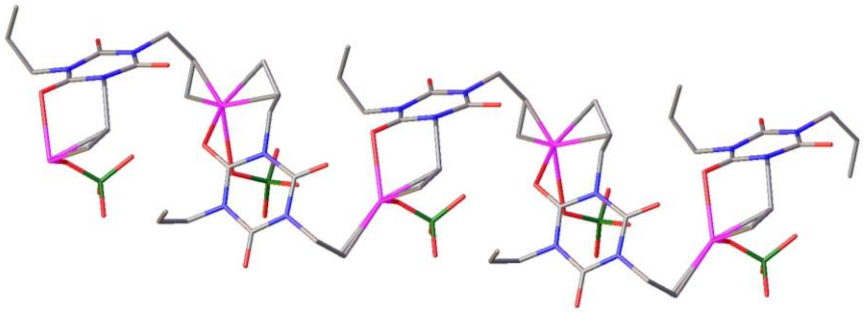


Figure 4.29 *– Part of the 1D polymeric assembly of the complex of ligand* ***4.6*** *with silver(I) perchlorate. All hydrogen atoms have been omitted for clarity. (Reprinted from reference [124]).*

From the four silver(I) complexes of ligand **4.6**, the complexes with the non-coordinating type counter anions (BF_4^- and PF_6^-) have the “trans-coordination mode”. The complexes with the coordinating type counter anions (NO_3^- and ClO_4^-) have the “cis-coordination mode”. Interestingly, ligand **4.6** so far has four different complexes with silver and in all of them only two of the allyl arms are coordinated with silver, but its isomer triallyl cyanurate produced only one silver(I) complex. This complex is formed with silver perchlorate and involves the coordination of all of the three allyl arms and the nitrogen atoms from the triazine ring. The structure is a 1D polymeric assembly, in which the perchlorate counter anion acts in a bidentate bridging fashion by coordinating with two neighbouring silver atoms, as shown in Figure 4.30.[124]

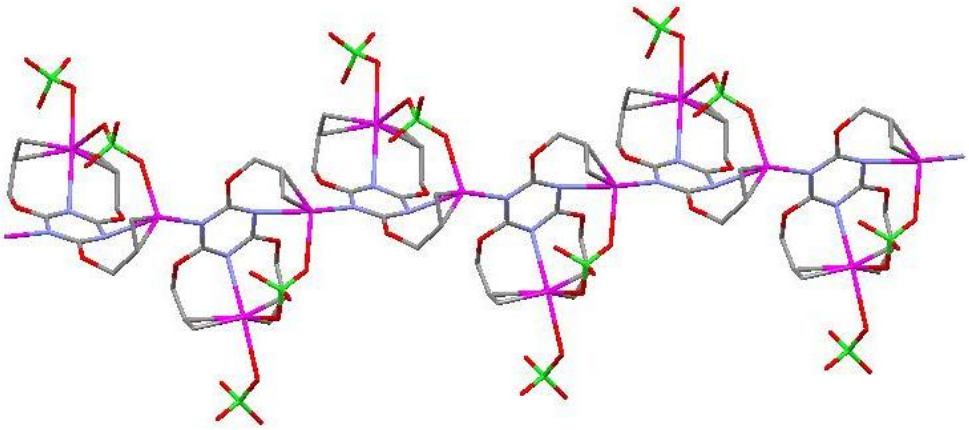


Figure 4.30 *- Part of the complex of triallyl cyanurate (isomer of ligand **4.6**) with silver(I) perchlorate. All hydrogen atoms have been omitted for clarity. (Reprinted from reference[124]).*

*4.8 Complexes of 1,1,3,3-tetraallylurea (**4.16**)*

With silver(I) perchlorate (**4.31**)

Ligand **4.16** was mixed with two equivalents of silver(I) perchlorate in acetone. Diethyl ether diffusion into the reaction mixture resulted in the growth of crystals suitable for X-ray crystal structure analysis. The structure was solved in the orthorhombic $P2_12_12$ space group. The asymmetric unit of the structure contains half a ligand molecule coordinating through one of the alkene functional groups of the allyl arm and the carbonyl oxygen, one silver atom and a coordinated perchlorate anion, revealing a 1:2 (ligand:metal) ratio or an M_2L_1 type coordination complex, as shown in Figure 4.31.

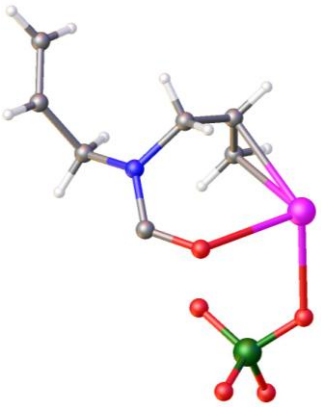


Figure 4.31 *– The asymmetric unit of complex **4.31**.*

The structure grows into a 1D ladder type polymeric structure through the coordination of the alkene functional group of the allyl arms to four different silver atoms. The carbonyl oxygen of the ligand is also coordinated with two silver atoms. The ligand is acting in a hexadentate manner by using all of its potential binding sites. Ligand **4.16** acts in both bridging and chelating modes. The coordination of the four allyl arms with four different silver atoms (Ag1, Ag1A, Ag1B, Ag1C), and also the carbonyl oxygen bridging two silver atoms (Ag1 and Ag1A) showed the bridging character of the ligand molecule. Ag1 and Ag1A are doubly bridged by the ligand through the coordination of the olefinic carbons (C1=C2 and C1A=C2A) and the carbonyl oxygen (O5). The coordination of the carbonyl oxygen (O5) and the allyl arm of the ligand through the olefinic carbons (C1=C2) with a single silver atom (Ag1), shows the ligand molecule also acts in a chelating manner, as shown in Figure 4.32.

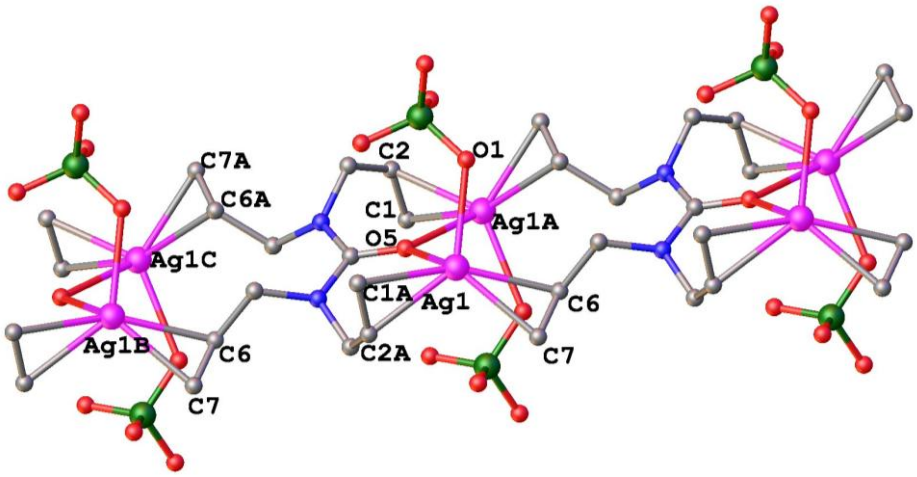
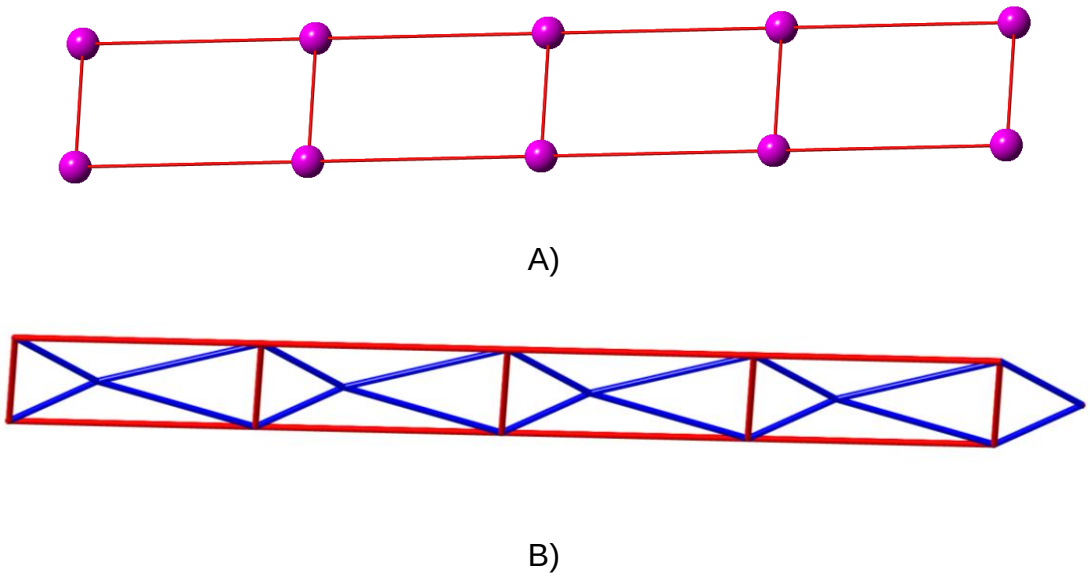


Figure 4.32 *– Part of the 1D polymeric assembly of complex* ***4.31****. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C1A 2.410(2), Ag1-C2A 2.458(2), Ag1-C1A,C2A 2.340(2), Ag1-O5 2.568(1), Ag1-O1 2.410(1), Ag1-C6 2.413(2), Ag1-C7 2.397(2), Ag1-C6,C7 2.309(2), C1A-Ag1-O5 89.2(2), C2A-Ag1-O5 81.9(2), C1A,C2A-Ag1-O5 85.3(2), C1A-Ag1-O1 102.0(2), C2A-Ag1-O1 131.9(2), C1A,C2A-Ag1-O1 117.3(2), O5-Ag1-O1 86.0(4), C1A-Ag1-C6 156.2(2), C1A-Ag1-C7 123.7(2), C2A-Ag1-C6 129.9(2), C2A-Ag1-C7 101.4(2), C1A,C2A-Ag1-C6,C7 128.7(2), O5-Ag1-C6*

104.7(2), O5-Ag1-C7 121.7(4), O5-Ag1-C6,C7 113.6(2), O1-Ag1-C6 98.1(2), O1-Ag1-C7 124.3(2), O1-Ag1-C6,C7 111.5(2).

The silver atom is four coordinate with two olefinic groups of the allyl arms, one carbonyl oxygen atom of the ligand and one oxygen atom from the perchlorate counter anion. The largest bond angle around silver is between the centroids of the coordinated olefinic allyl arms (C1A,C2A-Ag1-C6,C7) 128.7°, and the second largest angle is between the oxygen atom of the perchlorate anion and the centroid of one of the coordinated allyl arms (C1A,C2A-Ag1-O1) 117.3°. The calculated τ_4 value for silver is 0.81, revealing a trigonal pyramidal shape. The bond distance between the carbonyl oxygen and the two symmetry related silver atoms (O5-Ag1 and O5-Ag1A) is equal (2.568 Å). This distance is longer than the perchlorate counter anion oxygen atom coordinated with silver (O1-Ag1) 2.410 Å. The longer bond distance of the O5-Ag1 may be related to the contribution of all of the lone pair electrons of O5 for the coordination, while the perchlorate oxygen (O1) uses only one lone pair of electrons. Ligand **4.16** bridges silver atoms with two different separation distances. The double bridged silver atoms separation distance (Ag1-Ag1A, 4.230 Å) is shorter than the separation distance measured for Ag1-Ag1B (7.854 Å). The perchlorate anions coordinate in a monodentate fashion positioning above and below the plane of the 1D polymeric assembly, as shown in Figure 4.32. An interesting feature of this structure is the way the alkene functional groups orient around the silver atoms. If we see the orientation of C1=C2 in Figure 4.32, it is downward, while the C1A=C2A is oriented in the opposite direction, or upwards relative to the C1=C2 orientation. The same thing goes for the orientations of C6=C7 and C6A=C7A. This orientation could be explained as a “trans-coordination mode”. In general, the ligand molecule is flexible enough to accommodate the coordination of all of the allyl arms as well as the carbonyl oxygen. Considering the coordination of the silver atoms and the 1D polymeric nature of the complex the structure is a 1D ladder polymeric assembly, as shown in Figure 4.33.



A)

B)

Figure 4.33 *– A) The 1D ladder type polymer between the silver atoms in complex* ***4.31****. (The pink balls represent silver atoms) B). A simple presentation of the coordination in complex* ***4.31****. The blue lines represent the ligand molecule and the red lines represent the ladder structure formed between the silver atoms.*

With silver(I) triflate (**4.32**)

Ligand **4.16** was mixed with two equivalents of silver(I) triflate in acetone. Vapour diffusion of diethyl ether into the reaction mixture over a week resulted in the growth of block-like crystals suitable for single crystal structure analysis. The structure was solved in the monoclinic C2/c space group. The asymmetric unit contains half a ligand molecule coordinated through one of the allyl arms of the ligand, two silver atoms and two coordinated triflate counter anions, revealing a 1:4 (ligand:metal) ratio or an M_4L_1 type coordination complex. The $-CF_3$ group in one of the coordinated triflate anions has disorder over two positions with 70% dominant position occupancy, as shown in Figure 4.34. The structure grows into a 1D polymeric assembly through the coordination of all allyl arms and the carbonyl oxygen of the ligand with silver. The major player in this structure is the triflate counter anion. Each silver atom is coordinated with only one alkene functional group. The anion with the disordered $–CF_3$ group is coordinated with two silver atoms through one of the

oxygen atoms, while the other triflate anion is coordinated with three different silver atoms using all three of the oxygen atoms.

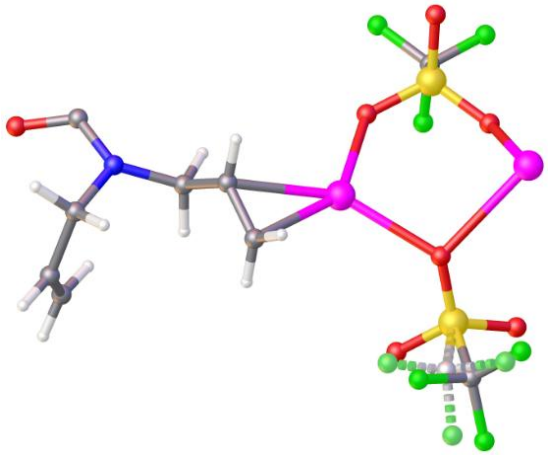
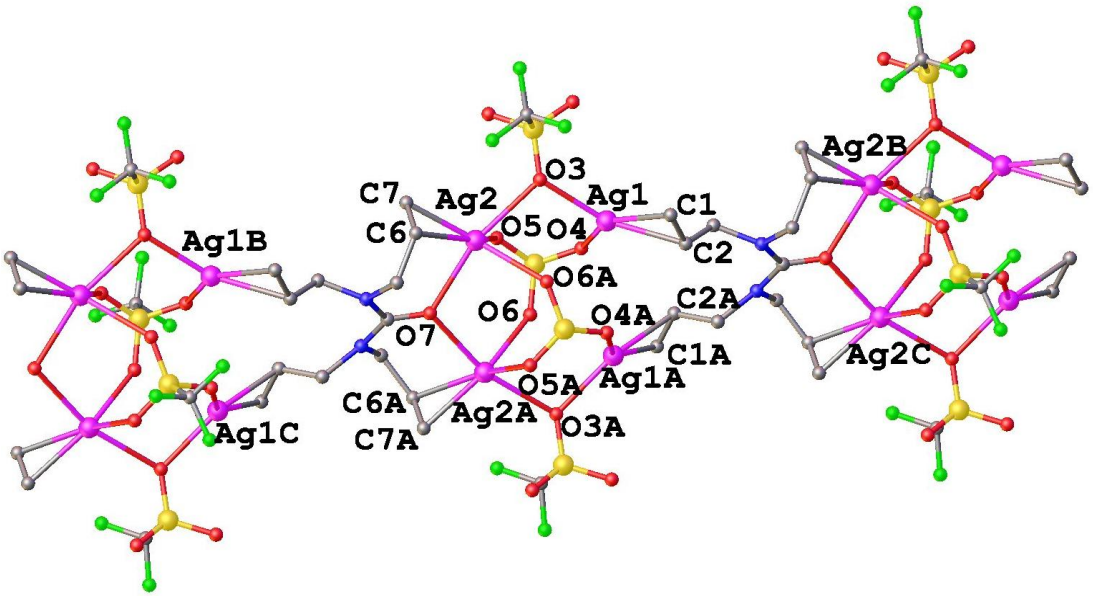


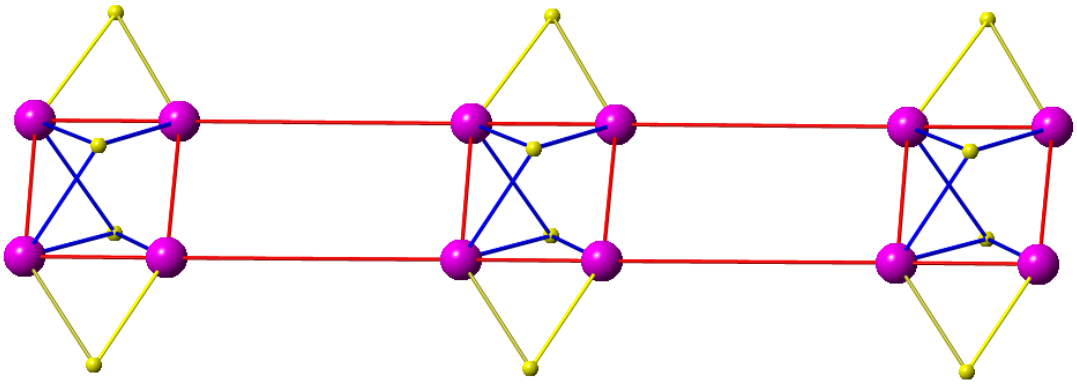
Figure 4.34 *– The asymmetric unit of complex* ***4.32****. The disorder in the triflate anion is shown with light colour and broken bonds.*

The disordered triflate anions coordinated to silver are in the plane of the polymer but they are oriented in opposite directions. However, the triflate anion without disorder is coordinated to silver from the top and bottom of the plane of the 1D polymer, which keeps the $–CF_3$ group far apart to minimize the steric clash between them. This coordination creates two types of silver atoms in the structure. One of them is five coordinate from the coordination of one allyl arm, one carbonyl oxygen atom of the ligand, one from the coordination of the disordered triflate anion and two from the other triflate anion with a distorted pyramidal shape. The second is a three coordinate silver atom from the coordination of one alkene functional group, one carbonyl oxygen atom of the ligand and one from the disordered triflate anion with a distorted trigonal geometry, as shown in Figure 4.35. The ligand acts in a bridging and chelating manner, as observed in complex **4.31**. It bridges the silver atoms (Ag2-Ag2A) through the coordination of the carbonyl oxygen (O7) atom and the alkene functional groups of the allyl arms (C6=C7 and C6A=C7A) with a separation distance of 4.063 Å. The coordination of O7 and the C=C double bond (C6,C7) from the same ligand molecule with Ag2 represents chelating coordination. The ligand molecule bridges Ag2 and Ag1B

with a separation distance of 7.741 Å, which is shorter than the separation distance observed in complex **4.31** (7.854 Å). The ligand molecule also bridges Ag1 and Ag1A through the coordination of the allyl arms with a separation distance of 4.307 Å. The triflate anions bridge Ag1A and Ag2A with different separation distances of 3.784 Å and 5.634 Å.



A)



B)

Figure 4.35 *– A) Part of the polymeric structure of complex* ***4.32*** *showing the coordination of the two types of triflate counter anions. All hydrogen atoms, the disorder from the triflate anion and some of the –CF_3 groups have been omitted for clarity. B) Simple representation of the complex. Pink balls represent*

silver; yellow balls represent the triflate anion. The blue lines show the tridentate coordination of the triflate anion. The yellow lines represent the bidentate coordination of the disordered triflate anion. Selected bond lengths(Å) and angles(°): Ag1-C1 2.312(4), Ag1-C2 2.380(3), Ag1-C1,C2 2.248(4), Ag1-O3 2.314(2), Ag1-O4 2.345(3), Ag2-O3 2.514(2), Ag2-O5 2.372(3), Ag2-O6A 2.443(3), Ag2-C6A 2.399(3), Ag2-C7A 2.346(3), Ag2-C6A,C7A 2.276(3), Ag2-O7 2.501(2), C1-Ag1-O3 116.0(2), C2-Ag1-O3 149.2(2), C1,C2-Ag1-O3 132.8(2), C1-Ag1-O4 144.4(2), C2-Ag1-O4 111.3(2), C1,C2-Ag1-O4 127.6(2), O3-Ag1-O4 99.3(1), O3-Ag2-O5 83.6(1), O3-Ag2-O6A 72.4(2), O3-Ag2-C6 113.2(1), O3-Ag2-C7 106.0(1), O3-Ag2-C6,C7 110.5(1), O3-Ag2-O7 163.7(2), O5-Ag2-O6A 95.1(2), O5-Ag2-C6 148.6(1), O5-Ag2-C7 119.0(1), O5-Ag2-C6,C7 134.4(1), O5-Ag2-O7 86.6(2), O6A-Ag2-C6 114.8(1), O6A-Ag2-C7 145.7(1),O6A-Ag2-C6,C7 130.3(1), O6A-Ag2-O7 95.6(2), C6-Ag2-O7 81.6(2), C7-Ag2-O7 90.1(1), C6,C7-Ag2-O7 85.6(1).

As in complex **4.31**, the “trans-coordination mode” of the allyl arms with silver is observed. The oxygen-silver bond distances are all in the expected range but the oxygen atoms coordinated with two silver atoms have longer bond lengths relative to others. The oxygen atom (O3) from the disordered triflate anion bridges two crystallographically independent silver atoms with different bond lengths. The bond distance in Ag1-O3 (2.314 Å) is shorter than the bond distance in Ag2-O3 (2.514 Å). The carbonyl oxygen atom (O7) from the ligand molecule bridges two symmetry related silver atoms Ag2 and Ag2A with the same bond length (Ag2-O7 and Ag2A-O7) 2.501 Å.

With silver(I) tetrafluoroborate (**4.33**)

Ligand **4.16** was mixed with two equivalents of silver(I) tetrafluoroborate solution in acetone. The same crystal growth method was used as in complexes **4.31** and **4.32**. The structure was solved in a higher symmetry orthorhombic Fdd2 space group. The asymmetric unit contains half a ligand

molecule, one silver atom, a non-coordinated tetrafluoroborate anion with disorder, a coordinated water molecule, and a non-coordinated water molecule, as shown in Figure 4.36. The dominant position occupancy for the disordered tetrafluoroborate anion is 60%. The structure grows into a 1D polymeric assembly through the coordination of all four of the allyl arms and the carbonyl oxygen atom of the ligand, just like complex **4.31**.

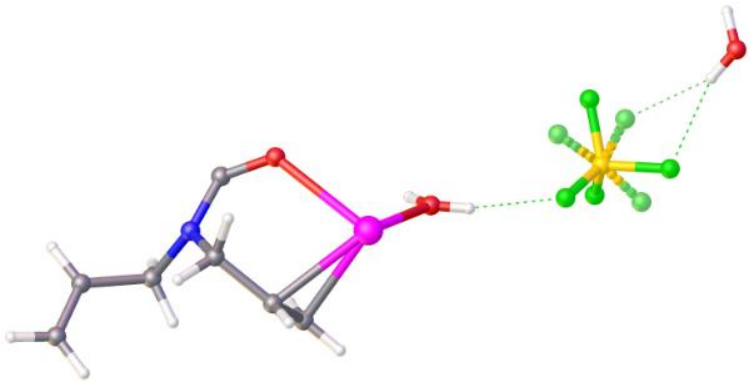


Figure 4.36 *– The asymmetric unit of complex* ***4.33****. The tetrafluoroborate anion is disordered over two positions with 60% dominant occupancy. The disorder in the anion is shown with broken bonds.*

The ligand acts in a hexadentate manner by coordinating through all of the potential coordination sites. The silver atom is four coordinate through the coordination of two olefinic groups, the carbonyl oxygen atom of the ligand and a water molecule. The largest bond angle around silver is between the centroids of coordinated allyl arms (C1,C2-Ag1-C6A,C7A) 128.9° and the second largest angle is between the oxygen atom from the coordinated water molecule and the alkene functional group of one of the coordinated allyl arms (O2-Ag1-C6A,C7A) 112.7°. The calculated τ_4 value is 0.82 with a trigonal pyramidal shape. Similar to complexes **4.31** and **4.32** the ligand molecule acts as both a bridging and chelating ligand. Ag1 and Ag1A are doubly bridged by the ligand molecule through the coordination of both the olefin functional group and the carbonyl oxygen atom, as shown in Figure 4.37. The separation distance between Ag1 and Ag1A is 4.142 Å, which is similar to those observed in complexes **4.31** (4.230 Å) and **4.32** (4.063 Å). The separation

distance measured between Ag1 and Ag1B is 7.897 Å, which is slightly longer than in complexes **4.31** (7.854 Å) and **4.32** (7.741 Å). The bond length measured in the coordination of the oxygen atom from the water molecule (Ag1-O2) 2.277 Å is shorter than the silver oxygen bond length from the carbonyl oxygen of the ligand molecule (Ag1-O1) 2.574 Å. This bond length is longer than the previous complexes (**4.31** and **4.32**) with bond lengths of 2.568 Å and 2.501 Å, respectively. All the silver carbon bond lengths are in the expected bond length range for such interactions.

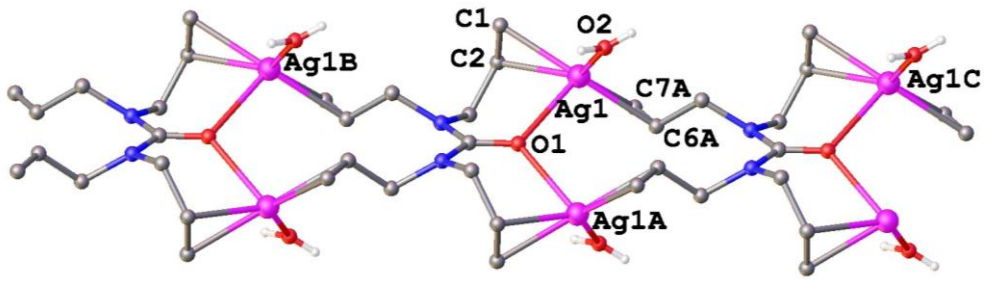


Figure 4.37 *– Part of the 1D polymeric structure of complex* ***4.33****. All of the tetrafluoroborate anion, the non-coordinated water molecule and the hydrogen atoms (except for the coordinated water molecule) have been omitted for clarity. Selected bond lengths(Å) and angles(°): Ag1-C1 2.399(2), Ag1-C2 2.449(2), Ag1-C1,C2 2.329(2), Ag1-O1 2.574(1), Ag1-O2 2.277(2), Ag1-C6A 2.427(2), Ag1-C7A 2.383(2), Ag1-C6A,C7A 2.309(2), C1-Ag1-O1 84.9(2), C2-Ag1-O1 79.4(1), C1,C2-Ag1-O1 81.8(2), C1-Ag1-O2 100.8(2), C2-Ag1-O2 131.8(2), C1,C2-Ag1-O2 116.6(2), O1-Ag1-O2 89.1(2), C1-Ag1-C6A 158.1(2), C1-Ag1-C7A 125.7(2), C2-Ag1-C6A 129.2(2), C2-Ag1-C7A 100.0(2), C1,C2-Ag1-C6A,C7A 128.9(2), O1-Ag1-C6A 104.8(2), O1-Ag1-C7A 117.6(2), O1-Ag1-C6A,C7A 111.9(2), O2-Ag1-C6A 99.0(2), O2-Ag1-C7A 126.2(2), O2-Ag1-C6A,C7A 112.7(2).*

The tetrafluoroborate counter anion and the non-coordinated water molecule have active roles in the stability and growth of the structure into a 2D polymeric assembly, as shown in Figure 4.38. The tetrafluoroborate has an intermolecular hydrogen bond with both the coordinated water molecule and

the non-coordinated one. Both water molecules also have other hydrogen bonding interactions. This leads to an interchain interaction between two ladders of the 1D polymeric assembly. Such intermolecular hydrogen bonding in a 2D structure has been observed previously in a 1,4-naphthalenedicarboxylate bridged coordination dimer with Cu(II) ions.[227]

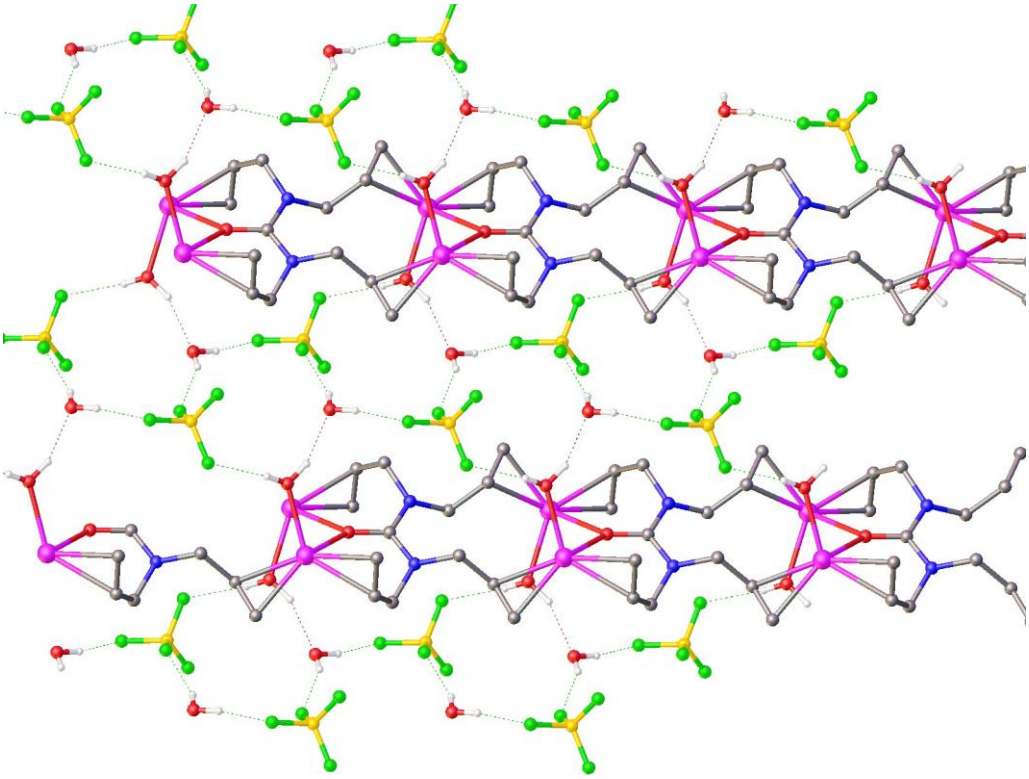


Figure 4.38 *– The 2D polymeric structure of complex* ***4.33*** *resulting from the intermolecular hydrogen bonding. All hydrogen atoms except on the water molecule and the disorder of the tetrafluoroborate counter anion have been omitted for clarity.*

D-H⋯A	D-H	H⋯A	D⋯A	D-H⋯A
O-H⋯O	0.881	1.851	2.693	159.02
O-H⋯F	0.781	1.976	2.743	167.73
O-H⋯F	0.856	1.995	2.786	153.12
O-H⋯F	0.816	2.063	2.848	161.25

Table 4.5 *Hydrogen bonding geometry with oxygen of water molecules and the tetrafluoroborate counter anion in complex 4.33*

4.9 Summary

This chapter covers the complexes of five ligands with different silver(I) salts and the synthesis of three ligands. One of these ligands is a new compound.

Complexes of **4.12** with silver triflate and silver tetrafluoroborate showed the formation of polymeric assemblies involving the coordination of the alkene functional group and the carbonyl oxygen of the ligand. In complex **4.22** one of the allyl arms, the carbonyl oxygen of the ligand and the triflate counter anion coordinated with silver through two oxygen atoms resulting in a 1D polymeric sheet. The polymeric sheets are interconnected through hydrogen bonding to give a 2D polymeric assembly. In complex **4.23** both allyl arms of the ligand and the carbonyl oxygen coordinated with silver to give a 1D helical structure. Having the flexibility of the ligand and the non-coordinating tetrafluoroborate counter anion helped in forming this helical assembly.

Complexes of ligand **4.13** with different silver salts gave different assemblies. With perchlorate and triflate anions 1D polymeric assemblies were obtained but with tetrafluoroborate and hexafluorophosphate anions discrete assemblies were formed. Complex **4.24** gave a 1D polymeric ladder type assembly through the coordination of the carbonyl oxygen and the allyl arms. The perchlorate anion coordinated with silver in a monodentate fashion.

Complex **4.25** gave a 1D zigzag polymeric assembly through the coordination of both allyl arms with silver. No coordination of the carbonyl oxygen was observed. Interestingly, a water molecule coordinated with silver instead of the triflate anion but the triflate anion has a weak hydrogen bond with the coordinated water molecule. In complexes **4.26** and **4.27** discrete binuclear assemblies were obtained through the coordination of both allyl arms and the carbonyl oxygen.

Complex **4.28** is a 1D ladder type polymeric assembly with silver triflate by coordinating through both allyl arms of ligand **4.15**, which acts as the side of the ladder, and the doubly bridging triflate anion acts as the rung of the ladder.

Complexes of **4.6** with silver hexafluorophosphate and silver nitrate gave polymeric assemblies using two allyl arms out of three for coordination. Complex **4.29** is a 1D polymer with hexafluorophosphate. The coordinated allyl arms are in a “trans-coordination mode” and a water molecule is coordinated to silver, which has a hydrogen bonding interaction with the hexafluorophosphate anion. Complex **4.30** is a 1D polymeric assembly with silver nitrate. Unlike complex **4.29**, the coordinated allyl arms are in a “cis-coordination mode”. The nitrate anion coordinated with silver in a monodentate mode.

Complexes of **4.16** with silver perchlorate, silver triflate and silver tetrafluoroborate gave polymeric assemblies involving the coordination of all of the allyl arms and the carbonyl oxygen. Complexes **4.31** and **4.32** gave 1D polymeric assemblies, while complex **4.33** gave a 2D polymeric assembly through hydrogen bonding.

In general, the carbonyl oxygen and the allyl arms are cooperative in coordination to silver. In all of the complexes the olefin group of the allyl arm coordinated with silver. It seems the olefin group is better at coordinating with silver than the carbonyl oxygen.

Chapter Five

Conclusion

Chapter Five

Conclusion and future directions

5.1 Conclusion

This thesis has covered the synthesis of thirty nine ligands, fourteen of which were previously unreported and the coordination chemistry of forty two ligands. Three of these ligands are commercially available. These ligands are classified into three major categories containing allyloxy, diallylamine and allyl groups.

The ligands containing allyloxy have the advantage of having some flexibility combined with ease of synthesis, as well as variation of the number of allyloxy arms within a ligand. The number of allyloxy arms within a ligand varied from one to six.

Ligands containing one allyloxy group have quinoline ring and azobenzene nitrogen atoms. These nitrogen atoms and the allyloxy arms of the ligand are coordinated with silver which resulted in discrete rectangular shaped assemblies, except for one which gave a 1D linear polymeric assembly.

In general, ligands containing two allyloxy groups are designed around a bisphenol moiety. This group of ligands gave 1D and 2D polymeric assemblies. The 1D polymeric assemblies resulted from the coordination of only the olefin group, while the 2D polymeric assemblies involve the coordination of either the carbonyl group or the aromatic ring of the ligand in addition to the olefin group.

Ligands containing three, four and six allyloxy arms also gave discrete, 1D or 2D polymeric assemblies. These assemblies are obtained either through the interaction of only the olefin groups or the combination of the aryl ring and other functional groups from the core of the ligand.

Two of the ligands containing four allyloxy arms gave discrete assemblies, which involve the coordination of two olefin groups with a single silver atom and either the counter anion or the aromatic ring to give M_2L or M_4L_2 type

coordination complexes. One of the ligands containing four allyloxy arms gave a rare 1D-1D polycatenane due to its long and flexible allyloxy arms that allowed the interpenetration of two ladders.

The complex obtained from the ligands containing six allyloxy groups involve the coordination of three alkene functional groups with a single silver atom, which does not have any interaction either from the aromatic ring or the counter anion.

Ligands containing diallylamine group were designed in the hope of achieving chelating coordination of two allyl arms from the same amine group with silver. The ligand design in this group encompasses changing the number of diallylamine groups within a single ligand (from one, two and three) to using spacer groups and also changing the core structures. The core structures of the ligand varied by using benzene, pyridine, pyrimidine, thiazole and triazine rings that give an insight on the influence of the core structure over the assembly of the complex. Nitrogen-containing heterocyclic cores can also be used to compare Ag-σ-donor coordination with nitrogen of the core and Ag-π-donor coordination with the olefin group.

Most of the ligands containing diallylamine group with a benzene core structure failed to grow crystals of complexes with any silver(I) salt. The complex of one ligand achieved our objective by chelating two allyl arms from the same amine group with a single silver atom.

Ligands containing N-heterocyclic cores grew crystals of complexes that involve the coordination of the nitrogen atom of the N-heterocyclic core and the olefin group. However, the interaction of the allyl arms from the same amine group is either bridging (for ligands containing one diallylamine group) or ‘atypical’ chelating coordination (for ligands containing two and three diallylamine group). Despite changes to the core structure, ligands containing one diallylamine group form 1D polymeric assemblies through the nitrogen atom and the olefin group of the ligand.

Ligands containing two and three diallylamine groups form discrete and 1D polymeric assemblies. In these structures the ligands used the allyl arms and

the nitrogen atom of the N-heterocycle for interaction with silver. High pyrimidalization of the nitrogen atoms of the N-heterocyclic ring as well as a better silver-nitrogen interaction relative to the silver-carbon of the benzene ring plays a significant role in the growth of the crystals of the complexes.

Ligands containing allyl arm with urea cores form discrete, 1D ladder or helical structures depending on the flexibility of the ligand and the type of counter anion involved. The carbonyl oxygen of the urea plays a significant role in determining the structure of the complex by coordinating with silver. In most of the complexes of the ligands containing urea, both the carbonyl oxygen atom and the olefin group of the ligand coordinated with silver; however, the olefin group seems preferred to the carbonyl oxygen atom.

Hydrogen bonding between hydrogen atoms of the –NH group of the urea and the oxygen or fluorine atoms of the counter anions transform some of the 1D polymeric sheets into 2D assemblies.

5.2 Future directions

Growing crystals of complexes of ligands containing two diallylamine groups with benzene core were unsuccessful and the reason is not known. In future developing methods of growing crystals of complexes for this group of ligands would be interesting. Solution studies might give clues about the optimum ligand to metal ratio that would result in a stable complex.

The study of this project solely made use of silver(I) salts; this could be further investigated by using other d^{10} metal atoms like Cu(I), Au(I) and Zn(II).

Mixed metal systems were not investigated in this project. Studying mixed metal systems, especially with ligands containing N-heterocyclic cores would give an opportunity to study the preference of different transition metal atoms towards a nitrogen atom and the olefin group; moreover, new materials with interesting properties might be produced.

Chapter Six

Experimental

Chapter six

Experimental

6.1 Preparation of ligands and ligand precursors

6.1.1 General information

Unless otherwise specified, all reagents and starting materials were reagent grade, purchased from standard suppliers and used as received. Where anhydrous solvents were required, the HPLC-grade solvent was either distilled from standard drying agents or dried by passing over a sealed column of activated alumina. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Elemental analysis was carried out by Campbell Microanalytical Laboratory, University of Otago.

Infrared spectroscopy

All infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR instrument operating in diffuse reflectance mode with samples prepared as KBr mulls (KBr), or in transmittance mode with liquid samples pressed between KBr discs (neat).

Nuclear Magnetic Resonance

All spectra were recorded on a Varian INOVA 500 or Varian Unity 300 instrument, operating at 500 and 300 MHz, respectively, for ^{1}H, and 125 and 75 MHz, respectively, for ^{13}C. All samples were dissolved in commercially available deuterated solvents d_6-DMSO, $CDCl_3$, CD_3CN. Spectra were referenced to the residual solvent peaks and/or TMS. COSY, HSQC, and HMBC experiments were employed where required, using standard Varian pulse sequences.

Mass spectrometry

Mass spectra were recorded by Dr Marie Squire and Dr Meike Holzenkaempfer on either a DIONEX Ultimate 3000 or Bruker MaXis 4G spectrometer, both of which were operated in high resolution positive ion

electrospray mode. Samples were dissolved and diluted to the required concentration in HPLC grade acetonitrile or methanol.

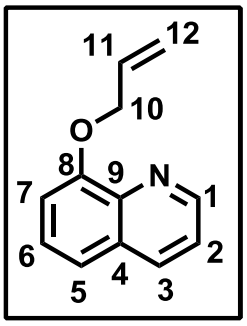
6.1.2 General procedure for the preparation of ligands containing allyloxy groups

Two different literature procedures were used for the synthesis of ligands containing allyloxy group. For those ligands synthesized from the combination of an aryl alcohol with allylbromide, Undheim's[142] method was used. One equivalent of allyl bromide was added to a mixture of one equivalent of aryl alcohol and potassium carbonate in 60 ml of acetone. The resulting solution was refluxed overnight and then filtered. The filtrate and acetone washings were collected and concentrated *in vacuo*. The remaining oil was treated with 60 ml of 1 M NaOH solution and the organic layer was extracted with 3x50 ml of diethyl ether. The organic extracts were combined and concentrated *in vacuo*.

For those ligands synthesized from the combination of bromomethylarene and allyl alcohol, Huang's[151] method was used. One equivalent of bromomethylarene was added to a mixture of one equivalent of allyl alcohol and NaH in 80 ml of dry tetrahydrofuran (THF). The resulting solution was refluxed over two days and then quenched with 10% ammonium chloride solution. The organic layer was extracted with 3x75 ml of ethyl acetate and washed with water and brine solution. The resulting solution was dried over $MgSO_4$ then concentrated *in vacuo*. Finally the target material was purified by column chromatography using silica gel (60 mesh, 200-300) and different ethyl acetate / petroleum ether solvent ratios.

*Preparation of 8-allyloxyquinoline (**2.10**)*

A mixture of 8-hydroxyquinoline (0.186 g, 1.28 mmol) and K_2CO_3 (0.177 g, 1.28 mmol) was stirred in acetone (30 ml). Allylbromide (0.11 ml, 1.28 mmol) was added to this mixture and refluxed overnight. The reaction was cooled to room temperature and the solid material was filtered off. Concentrating the solution *in vacuo* gave a yellow oily liquid. The oily liquid was washed with 60 ml of 1 M NaOH solution followed by 3x50 ml diethyl ether extraction. The organic extracts were combined and dried over $MgSO_4$.

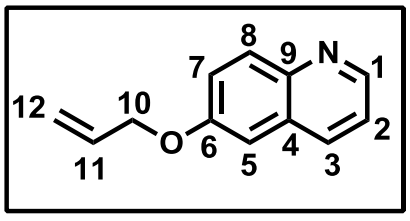


2.10

Diethyl ether was evaporated under reduced pressure to give crude **2.10** as a yellow oily liquid. Purification of the crude product with silica gel column chromatography using 30:70 (ethyl acetate:petroleum ether) solvent ratio gave (0.213 g, 90%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.87 (2H, d, J = 5.6 Hz, H10), 5.34 (1H, dd, J = 10.7, 1.3 Hz, H12), 5.48 (1H, dd, J = 17.3, 1.4 Hz, H12'), 6.19-6.25 (1H, m, H11), 7.08 (1H, d, J = 7.7 Hz, H7), 7.38-7.46 (3H, m, H2, H5, H6), 8.14 (1H, dd, J = 8.3, 1.3 Hz, H3), 8.96 (1H, dd, J = 4.2, 1.4 Hz, H1). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 70.08 C10, 109.55 C7, 118.60 C12, 119.94 C6, 121.84 C2, 126.89 C5, 129.72 C4, 133.37 C11, 136.35 C3, 140.39 C9, 149.48 C1, 154.41 C8. ESI-MS: found MNa^+ = 208.0730; $C_{12}H_{11}NONa$ requires MNa^+ = 208.0733. IR (cm^{-1}) 2923, 1647, 1615, 1596, 1570, 1500, 1472, 1425, 1377, 1317, 1262, 1183, 1104, 1078, 987, 928, 822.

*Preparation of 6-allyloxyquinoline (**2.12**)*

A mixture of 6-hydroxyquinoline (1.45 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol) was stirred in methanol (50 ml). Allylbromide (0.870 ml, 10 mmol) was added to this mixture and refluxed overnight. The reaction was cooled to room temperature and the solid material was filtered off. Concentrating the solution *in vacuo* gave a brown red oily liquid. The oily liquid was washed with 60 ml of 1 M NaOH solution followed by 3x50 ml diethyl ether extraction. The

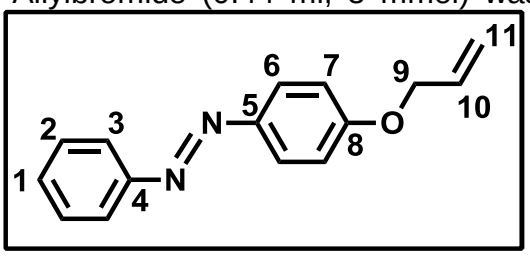


2.12

organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give crude **2.12** as a brown red oily liquid. Purification of the crude product with silica gel column chromatography using 30:70 (ethyl acetate:petroleum ether) solvent ratio gave (0.61 g, 33%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.65 (2H, d, J = 5.3 Hz, H10), 5.33 (1H, dd, J = 17.3, 1.5 Hz, H12'), 5.47 (1H, dd, J = 10.5, 1.3 Hz, H12), 6.07-6.15 (1H, m, H11), 7.00 (1H, s, H5), 7.34 (1H, dd, J = 8.3, 4.2 Hz, H2), 7.40 (1H, dd, J = 9.3, 2.9 Hz, H7), 7.39-7.41 (2H, m, H3,H8), 8.76 (1H, dd, J = 4.3, 1.7 Hz, H1). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 69.28 C10, 106.56 C5, 118.3 C12, 121.60 C2, 122.84 C7, 129.49 C4, 130.97 C8, 133.01 C11, 135.21 C3, 144.47 C9, 148.10 C1, 156.91 C6. ESI-MS: found MNa^+ = 208.0731; $C_{12}H_{11}NONa$ requires MNa^+ = 208.0733. IR (cm^{-1}) 2923, 1647, 1622, 1595, 1576, 1501, 1461, 1424, 1380, 1323, 1263, 1227, 1171, 1114, 999, 921, 833.

*Preparation of 4-allyloxyazobenzene (**2.14**)*

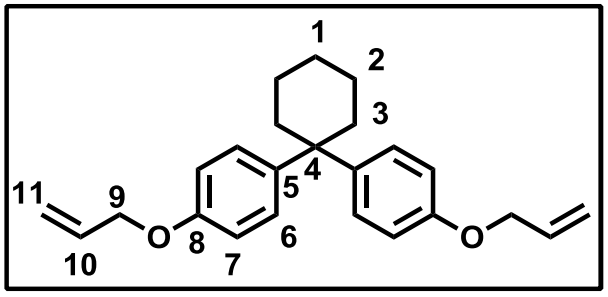
A mixture of 4-hydroxyazobenzene (0.99 g, 5 mmol) and K_2CO_3 (0.61 g, 5 mmol) was stirred in acetone (40 ml). Allylbromide (0.44 ml, 5 mmol) was added to this mixture and refluxed overnight. The reaction was cooled to room temperature and the solid material was filtered off. Concentrating the solution *in vacuo* gave an impure bright red powder. Purification of the crude product with silica gel column chromatography using 20:80 (ethyl acetate:petroleum ether) solvent ratio gave **2.14** as a brick red powder (0.95 g, 80%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.63 (2H, d, J = 5.1 Hz, H9), 5.34 (1H, d, J = 10.5 Hz, H11), 5.46 (1H, d, J = 17.2 Hz, H11'), 6.05-6.12 (1H, m, H10), 7.02-7.05 (2H, m, H7), 7.43-7.52 (3H, m, H1, H2), 7.88-7.94 (4H, m, H3, H6). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 69.26 C9, 115.19 C7, 118.32 C11, 122.81 C3,C6, 124.97 C6,C3, 129.28 C2, 130.63 C1, 132.98 C10, 147.30 C4, 152.99 C5, 161.29 C8. ESI-MS: found MNa^+ = 261.1001; $C_{15}H_{14}N_2ONa$ requires MNa^+ = 261.0998. IR (cm^{-1}) 3066, 2890, 1906, 1648, 1602, 1500, 1443, 1409, 1298, 1256, 1144, 1113, 1070, 998, 925, 838, 766, 722, 690, 551.



2.14

*Preparation of the diallylether of bisphenol Z (**2.20**)*

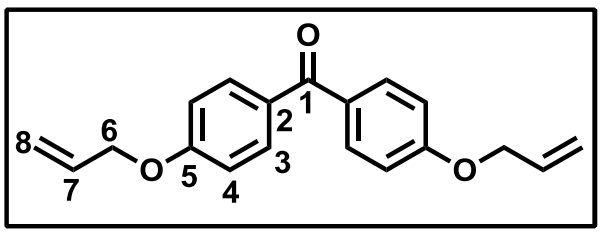
A mixture of bisphenol Z (1.25 g, 4.66 mmol), allylbromide (0.81 ml, 9.32 mmol), K_2CO_3 (1.29 g, 9.32 mmol) in acetone (50 ml) was refluxed overnight. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a yellow oily liquid. The oily liquid was washed with 60 ml of 1 M NaOH solution and **2.20** was extracted with 3x50 ml diethyl ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give pure **2.20** as a yellow oily liquid (0.99 g, 60.9%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 1.53-1.60 (6H, m, H1,H2), 2.26-2.28 (4H, m, H3), 4.54 (4H, d, J = 5.3 Hz, H9), 5.31 (2H, dd, 10.5, 1.1 Hz, H11), 5.45 (2H, dd, J = 17.2, 1.4 Hz, H11'), 6.07-6.12 (2H, m, H10), 6.88 (4H, d, J = 8.8 Hz, H7), 7.22 (4H, d, J = 8.9 Hz, H6). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 23.22 C2, 26.74 C1, 37.71 C3, 45.35 C4, 69.02 C9, 114.55 C7, 117.79 C11, 128.36 C6, 133.83 C10, 141.48 C5, 156.50 C8. ESI-MS: found MNa^+ = 371.1979; $C_{24}H_{28}O_2Na$ requires MNa^+ = 371.1982. IR(cm^{-1}) 3038, 2935, 2858, 1648, 1607, 1579, 1508, 1454, 1424, 1408, 1360, 1287, 1245, 1183, 1114, 1026, 997, 926, 897, 824.



2.20

*Preparation of 4,4'-di(allyloxy)benzophenone (**2.21**)*

A mixture of 4,4'-dihydroxybenzophenone (1.07 g, 5 mmol), K_2CO_3 (1.38 g, 5mmol) and allylbromide (0.87 ml, 10 mmol) in acetone (60 ml) was refluxed overnight. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a white powder. The white powder was dissolved in diethyl ether (50 ml) and washed with aqueous NaOH solution (50 ml). The organic layer was dried over $MgSO_4$ and

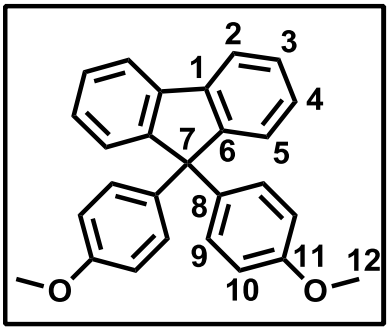


2.21

concentrated under reduced pressure to give a white powder. Recrystallization of the white powder from boiling absolute alcohol gave pure white crystals of **2.21** (0.92 g, 62.5%), m.p. 90-92^{o}C (lit. 76-78^{o}C[144]). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.62 (4H, d, J = 5.3 Hz, H6), 5.33 (2H, dd, J = 17.3, 1.4 Hz, H8'), 5.44 (2H, dd, J = 10.4, 0.9 Hz, H8), 6.04-6.10 (2H, m, H7), 6.97 (4H, d, J = 8.8 Hz, H4), 7.78 (4H, d, J = 8.8 Hz, H3). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 69.14 C6, 114.41 C4, 118.41 C8, 131.07 C2, 132.44 C3, 132.84 C7, 162.08 C5, 194.67 C1, which matches the literature values.[228] ESI-MS: found MNa^+ = 317.1143; $C_{19}H_{18}O_3Na$ requires MNa^+ = 317.1148. IR (cm^{-1}) 2930, 1636, 1602, 1502, 1416, 1366, 1293, 1254, 1176, 1150, 1119, 1017, 934, 853, 764.

*Preparation of 9,9-bis(4-methoxyphenyl)fluorene (**2.24**)*

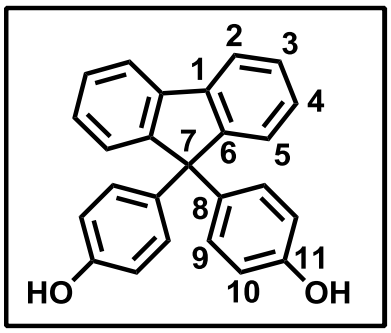
A literature method was adopted to synthesize **2.24**.[147] Under vigorous stirring concentrated sulfuric acid (20 ml, 0.40 mol) was added to glacial acetic acid (30 ml, 0.51 mol). After cooling the mixture to 15^{o}C, a mixture of anisole (27.3 ml, 0.25 mol) and fluoren-9-one (9.0 g, 0.05 mol) was added dropwise at the given temperature. Stirring was continued at room temperature for 5 days. The mixture was added to water and was extracted with 4x50 ml diethyl ether. The ethereal extract was washed free from acid with aqueous sodium hydrogen carbonate and water, dried over $MgSO_4$ and evaporated under reduced pressure to give the crude product as an oily liquid which was subjected to steam distillation in order to free it from anisole. Recrystallization from ethanol yielded **2.24** as colorless crystals (11.0 g, 58.2%), m.p. 95-97^{o}C (lit. m.p. 126^{o}C[147]). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 3.75 (6H, s, H12), 6.76 (4H, d, J = 8.8 Hz, H10), 7.13 (4H, d, J = 9.0 Hz, H9), 7.27-7.28 (2H, m, H4), 7.33-7.39 (4H, m, H3,H5), 7.76 (2H, d, J = 7.4 Hz, H2). Elem. Anal. found: C, 85.58; H, 5.98. Calc. for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. ESI-MS: found M^+ = 378.1614; $C_{27}H_{22}O_2$ requires M^+ = 378.1614.



2.24

*Preparation of 9,9'-bis(4-hydroxyphenyl)fluorene (**2.25**)*

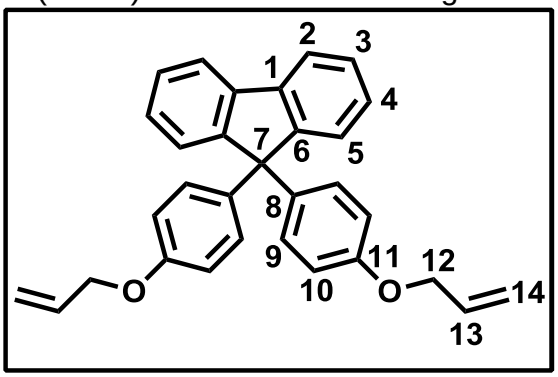
A solution of boron tribromide (1.40 ml, 14.8 mmol) in dry dichloromethane (35.0 ml) was added to a solution of **2.24** (1.4g, 3.7 mmol) in dry dichloromethane (50.0 ml) at -15^{o}C. The mixture was allowed to warm to room temperature, stirred for two days, hydrolyzed with ice-water, extracted with 3x50 ml diethyl ether, washed free from acid ($NaHCO_3$, water) and dried over $MgSO_4$. Concentrating the ethereal extract *in vacuo* gave an impure white powder. Recrystallization from ethanol yielded **2.25** as colorless crystals (1.24 g, 95.6%), m.p. 189-191^{o}C (lit. m.p. 115^{o}C[147]). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 6.68 (4H, d, J = 9.0 Hz, H10), 7.07 (4H, d, 9.0 Hz, H9), 7.25-7.28 (2H, m, H4), 7.33-7.38 (4H, m, H3,H5), 7.75 (2H, d, J = 7.5 Hz, H2).



2.25

*Preparation of 9,9'-bis(4-allyloxyphenyl)fluorene (**2.26**)*

A mixture of **2.25** (1.52 g, 4.3 mmol), allylbromide (0.76 ml, 8.69 mmol) and K_2CO_3 (1.20 g, 8.69 mmol) in acetone (60 ml) was refluxed overnight. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a light yellow oily liquid. The oily liquid was washed with 60 ml of 1 M NaOH solution and **2.26** was extracted with 3x50 ml diethyl ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give impure **2.26** as a light yellow oily liquid. Purification of the crude product using silica gel column chromatography with 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **2.26** as a colourless semi-solid material (1.52 g, 82%), m.p. 58-60^{o}C. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.47 (4H, d, J = 5.4 Hz, H12), 5.26 (2H, dd, J = 10.4, 1.3 Hz, H14), 5.38 (2H, dd, J

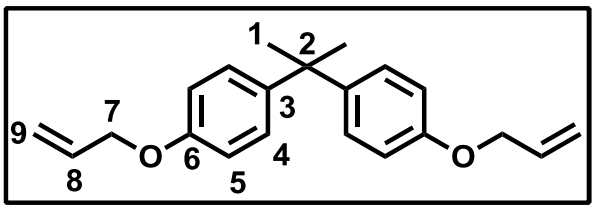


2.26

= 17.2, 1.6 Hz, H14'), 5.99-6.07 (2H, m, H13), 6.76 (4H, d, J = 9.0 Hz, H10), 7.11 (4H, d, J = 8.9 Hz, H9), 7.25-7.28 (2H, m, H4), 7.33-7.39 (4H, m, H3,H5), 7.76 (2H, d, J = 7.6 Hz, H2). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 64.37 C7, 69.01 C12, 114.49 C10, 117.93 C14, 120.36 C5, 126.27 C4, 127.55 C3, 127.91 C2, 129.38 C9, 133.57 C13, 138.49 C6, 140.17 C8, 152.00 C1, 157.56 C11. Elem. Anal. found: C, 86.58; H, 6.09. Calc. for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09. ESI-MS: found M^+ = 430.1931; $C_{31}H_{26}O_2$ requires M^+ = 430.1927. IR (cm^{-1}): 3017, 2886, 1853, 1649, 1582, 1606, 1506, 1447, 1411, 1382, 1291, 1242, 1178, 1117, 1017, 993, 923, 822, 749, 731, 648, 632.

*Preparation of the diallylether of bisphenol A (**2.27**)*

A mixture of bisphenol A (1.14 g, 5.0 mmol), allylbromide (0.87 ml, 10.0 mmol), K_2CO_3 (1.2 g, 10 mmol) in acetone (50 ml) was refluxed overnight. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a yellow oily liquid. The oily liquid was washed with 60 ml of 1 M NaOH solution and **2.27** was extracted with 3x50 ml diethyl ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give pure **2.27** as a yellow oily liquid (1.25 g, 80%). NMR values are consistent with the literature.[145] ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 1.62 (6H, s, H1), 4.49 (4H, d, J = 5.2 Hz, H7), 5.26 (2H, ddt, J = 17.2, 3.2, 1.5 Hz, H9'), 5.39 (2H, ddt, J = 10.5, 2.8, 1.3 Hz, H9), 6.00-6.08 (2H, m, H8), 6.81 (4H, dd, J = 9.6, 2.7 Hz, H5), 7.12 (4H, dd, J = 9.6, 2.7 Hz, H4). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 31.32 C1, 41.94 C2, 69.05 C7, 114.31 C5, 117.80 C9, 127.97 C4, 133.78 C8, 143.53 C3, 156.70 C6. IR (cm^{-1}) 2966, 2869, 1648, 1607, 1580, 1509, 1247, 1181, 1024, 828.

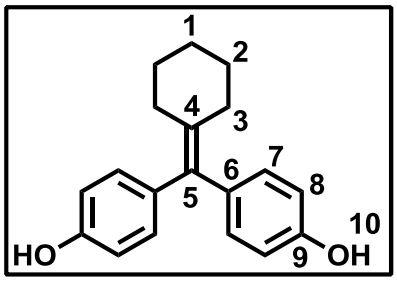


2.27

*Preparation of (cyclohexylidenedi(4-hydroxyphenyl))methane (**2.30**)*

Compound **2.30** was prepared using a literature procedure.[148] $TiCl_4$ (6.2 ml, 56 mmol) was added dropwise under nitrogen to a stirred suspension of zinc

powder (8.20 g, 126 mmol) in dry THF (80 ml) at -50^{o}C. When the addition was complete, the mixture was warmed to room temperature and then refluxed for 2 hours. A solution of 4,4'-dihydroxybenzophenone (2.0 g, 9 mmol) and cyclohexanone (4.0 ml, 38 mmol) in dry THF (120 ml) was added to the cooled suspension of titanium reagent at 0^{o}C and the mixture was refluxed for 2 hours. The reaction was cooled to room temperature and quenched with aqueous K_2CO_3 (30 ml), filtered through Celite, and extracted with 3x30 ml ethyl acetate. The organic layer was washed with water, brine, dried over $MgSO_4$, and concentrated *in vacuo*.

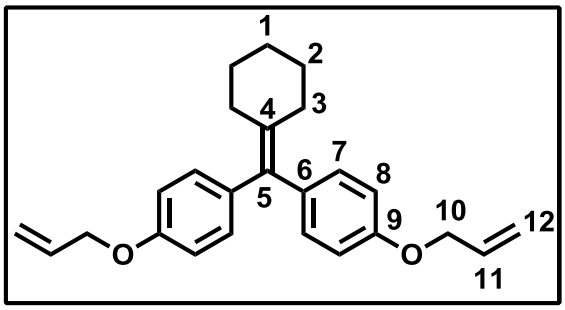


2.30

Silica gel column chromatography in 30:70 (ethyl acetate:petroleum ether) solvent ratio afforded **2.30** as a white powder (2.10 g, 83.2%), m.p. 223-225^{o}C. ^{1}H N.M.R. (500MHz, DMSO): δ 1.54-1.58 (6H, m, H1,H2), 2.18-2.20 (4H, m, H3), 6.70 (4H, d, J = 8.4 Hz, H8), 6.86 (4H, d, J = 8.4 Hz, H7), 9.31 (2H, s, H10). ESI-MS: found MH^+ = 281.1533; $C_{19}H_{21}O_2$ requires MH^+ = 281.1536.

*Preparation of cyclohexylidenedi(4-allyloxyphenyl)methane (**2.31**)*

A mixture of **2.30** (1.0 g, 3.6 mmol), K_2CO_3 (0.99 g, 7.13 mmol), allylbromide (0.62 ml, 7.13 mmol) in acetone (80 ml) was refluxed overnight. The reaction mixture was cooled to room temperature and the solid material was filtered off.



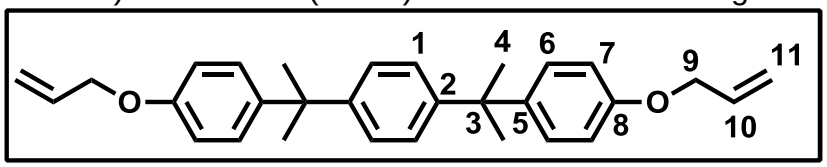
2.31

Concentrating *in vacuo* gave a white powder. Silica gel column chromatography in 20:80 (ethyl acetate:petroleum ether) solvent ratio afforded **2.31** as a white powder (0.95 g, 72.8%), m.p. 45-47^{o}C. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 1.56-1.59 (6H, m, H1,H2), 2.22-2.25 (4H, m, H3), 4.51 (4H, d, J = 5.3 Hz, H10), 5.27 (2H, d, J = 10.6 Hz, H12), 5.41 (2H, d, J = 17.2 Hz, H12'), 6.02-6.10 (2H, m, H11), 6.82 (4H, d, J = 8.5 Hz, H8), 7.01 (4H, d, J = 8.3 Hz, H7). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 27.11 C1, 28.94 C2, 32.74 C3, 69.02

C10, 114.21 C8, 117.83 C12, 131.11 C7, 133.67 C11, 133.70 C6, 136.28 C4, 138.59 C5, 157.10 C9. Elem. Anal. found: C, 83.15; H, 7.96. Calc. for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. ESI-MS: found MH^+ = 361.2161; $C_{25}H_{29}O_2$ requires MH^+ = 361.2162. IR (cm^{-1}): 2922, 2851, 1890,1651, 1605, 1571, 1507, 1455, 1426, 1362, 1174, 1112, 1020, 997, 918, 880, 839, 800, 736.

*Preparation of the diallylether of bisphenol P (**2.32**)*

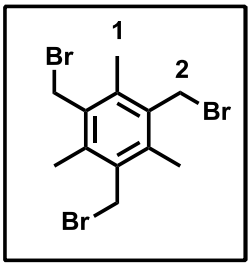
A mixture of bisphenol P (1.73 g, 5 mmol), allylbromide (0.87 ml, 10 mmol), K_2CO_3 (1.22 g, 10 mmol) in acetone (60 ml) was refluxed over night. The reaction mixture was cooled to room temperature and the solid material was filtered off. Concentrating *in vacuo* gave a colourless oily liquid. Washing the oily liquid with aqueous NaOH solution (60 ml, 1 M) gave a white precipitate. The precipitate was collected by filtration. Recrystallization from acetone gave **2.32** as a white crystalline material (1.90 g, 89%), m.p. 54-56°C. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 1.65 (12H, s, H4), 4.52 (4H, d, J = 5.2 Hz, H9), 5.28 (2H, dd, J = 10.4, 1.3 Hz, H11), 5.42 (2H, dd, J = 17.2, 1.7 Hz, H11'), 6.03-6.11 (2H, m, H10), 6.83 (4H, d, J = 8.8 Hz, H7), 7.12 (4H, s, H1), 7.16 (4H, d, J = 8.8 Hz, H6). ^{13}C N.M.R. ($CDCl_3$): δ 31.15 C4, 42.10 C3, 69.04 C9, 114.26 C7, 117.80 C11, 126.46 and 128.01 C1,C6, 133.78 C10, 143.35 and 148.09 C2,C5, 156.67 C8. Elem. Anal. found: C, 84.16; H, 8.05. Calc. for $C_{30}H_{42}O_2$: C, 84.47; H, 8.03. ESI-MS: found MCs^+ = 559.1612; $C_{30}H_{34}O_2Cs$ requires MCs^+ = 559.1613. IR (cm^{-1}): 3019, 2970, 2533, 1896, 1650, 1607, 1581, 1511, 1458, 1424, 1357, 1285, 1242, 1185, 1150, 1119, 1087, 1020, 931, 829, 767, 731.



2.32

*Preparation of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (**2.41**)*

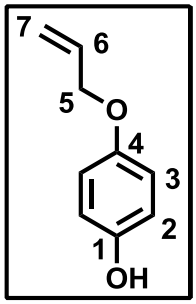
Compound **2.41** was prepared by a literature method.[149] A mixture of mesitylene (1.0 g, 0.01 mol), paraformaldehyde (2.0 g, 0.066 mol), $ZnBr_2$ (2.25 g, 0.01 mol), HBr/acetic acid (14 ml, 32.0%)



2.41

and glacial acetic acid (10 ml) was refluxed at 95^{o}C overnight and then poured into 60 ml of water. The product was filtered off on a G3 glass frit and dried in vaccum. Yield 3.45 g, 86.5%, m.p. 139-141^{o}C(lit. m.p. 183-186^{o}C.[229]) ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 2.47 (9H, s, H1), 4.58 (6H, s, H2).

*Preparation of 4-allyloxyphenol (**2.43**)*

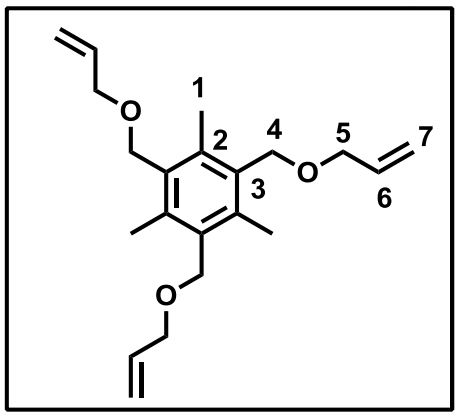


2.43

Compound **2.43** was synthesised using a literature method.[150] A mixture of hydroquinone (0.88 g, 8 mmol), allyl bromide (0.17 ml, 2 mmol), anhydrous K_2CO_3 (0.24 g, 2 mmol) and dried acetonitrile (20 ml) was refluxed for 12 hours. The reaction was cooled to room temperature and the white material was filtered off. Concentrating *in vacuo* gave a brown oily liquid. Flash column chromatography using 20:80 (ethyl acetate:petroleum ether) solvent ratio gave **2.43** as a brown oily liquid (0.275 g, 91.6%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.48 (2H, d, J = 5.4 Hz, H5), 5.28 (1H, dd, J = 10.5, 1.5 Hz, H7), 5.39 (1H, dd, J = 17.1, 1.5 Hz, H7'), 5.94-6.12 (1H, m, H6), 6.74-6.83 (4H, m, H2,H3).

*Preparation of 1,3,5-tris(allyloxymethyl)-2,4,6-trimethylbenzene (**2.45**)*

Allyl alcohol (0.41 ml, 6 mmol) was added dropwise to a mixture of **2.41** (0.80 g, 2 mmol) and NaH (0.14 g, 6 mmol) in dry THF (50.0 ml) at 0^{o}C. The mixture was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and the NaH was quenched with 30.0 ml of 1 M aqueous NH_4Cl solution, followed by 3x30 ml diethyl ether extraction. The organic layer was washed with water, brine and dried over $MgSO_4$. The diethyl ether was evaporated under reduced pressure to give a yellow oily liquid. Purification with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **2.45** as a yellow oily liquid (0.50 g, 76%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 2.42 (9H, s, H1), 4.04 (6H, d, J = 5.7

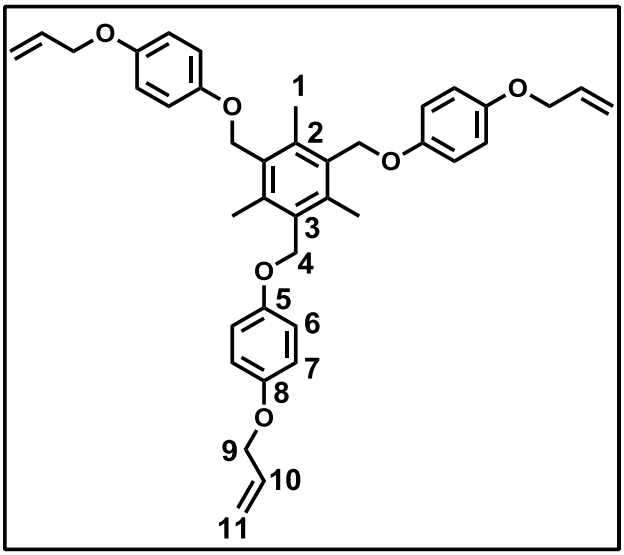


2.45

Hz, H5), 4.54 (6H, s, H4), 5.20 (3H, dd, J = 10.4, 1.6 Hz, H7), 5.31 (3H, dd, J = 17.2, 1.6 Hz, H7'), 5.94-6.00 (3H, m, H6). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 15.98 C1, 67.11 C4, 71.53 C5, 117.32 C7, 132.3 C2,C3, 135.31 C6, 138.45 C3,C2. ESI-MS: found MNa^+ = 353.2087; $C_{21}H_{30}O_3Na$ requires MNa^+ = 353.2091. IR (cm^{-1}): 3079, 3012, 2978, 2922, 2849, 1849, 1646, 1577, 1496, 1455, 1419, 1374, 1348, 1290, 1262, 1243, 1129, 1094, 1061, 1001, 923, 831.

*Preparation of 1,3,5-tris(4-allyloxyphenoxymethyl)-2,4,6-trimethylbenzene (**2.46**)*

4-Allyloxyphenol (**2.43**) (0.90 g, 6 mmol) was added to a mixture of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (**2.41**) (0.80 g, 2 mmol) and NaH (0.14 g, 6 mmol) in dry THF (100 ml) at 0^{o}C. The mixture was warmed to room temperature then refluxed for a week. The reaction was cooled to room temperature and NaH was quenched with 50.0 ml of 1 M aqueous NH_4Cl solution followed by 3x60 ml diethyl ether extraction. The organic layer was washed with water, brine and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give a yellow oily liquid. Purification with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **2.46** mixed with **2.41**. Recystalization of this mixture from ethanol gave **2.46** as white crystals (0.80 g, 66%), m.p. 60^{o}C. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 2.44 (9H, s, H1), 4.51 (6H, d, J = 5.3 Hz, H9), 5.04 (6H, s, H4), 5.28 (3H, dd, J = 10.5, 1.2 Hz, H11), 5.41 (3H, dd, J = 17.2, 1.5 Hz, H11'), 6.02-6.09 (3H, m, H10), 6.88 (6H, d, J = 8.9 Hz, H7), 6.95 (6H, d, J = 8.9 Hz, H6). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 15.88 C1, 65.58 C4, 69.53 C9, 115.52 and 115.73 C6,C7, 117.55 C11, 131.93 C2, 133.60 C10, 139.16 C3, 152.99 C5,C8,

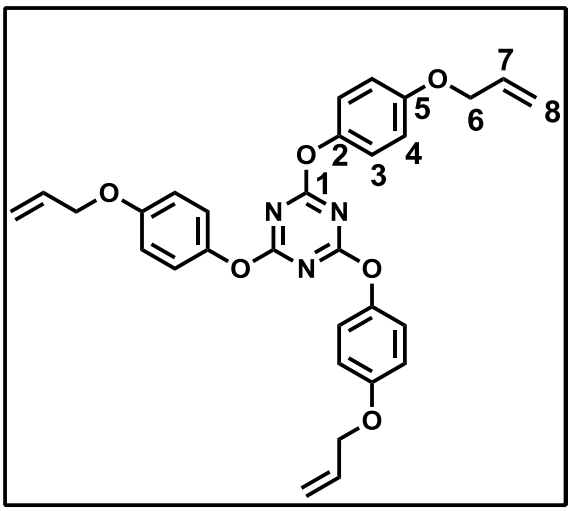


2.46

153.47 C8,C5. Elem. Anal. found: C, 77.17; H, 7.08. Calc. for $C_{39}H_{42}O_6$: C, 77.20; H, 6.98. ESI-MS: found M^+ = 606.2976; $C_{39}H_{42}O_6$ requires M^+ = 606.2980. IR (cm^{-1}): 2924, 2854, 1708, 1646, 1607, 1590, 1506, 1464, 1375, 1284, 1224, 1112, 1029, 997, 933, 821, 783, 747.

*Preparation of 2,4,6-tris(4-allyloxyphenoxy)-1,3,5-triazine (**2.48**)*

4-Allyloxyphenol (**2.43**) (0.09 g, 0.6 mmol) was added dropwise to a mixture of cyanuric chloride (0.037 g, 0.2 mmol) and K_2CO_3 (0.073 g, 0.6 mmol) in acetone (30 ml) at 0°C. The mixture was stirred at this temperature for an hour followed by two hours at room temperature. Finally the mixture was refluxed for 48 hours. The mixture was cooled to room temperature and the white material was filtered off. Concentrating the filtrate *in vacuo* gave a crude white powder. Purification of the crude product by column chromatography using petroleum ether as solvent gave pure **2.48** as a white powder (0.045 g, 43%), m.p. 125-127°C. ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.52 (6H, d, J = 5.1 Hz, H6), 5.30 (3H, dd, J = 10.5, 1.5 Hz, H8), 5.41 (3H, dd, J = 17.1, 1.5 Hz, H8'), 6.87 (6H, d, J = 9.3 Hz, H4), 7.04 (6H, d, J = 9.0 Hz, H3). Elem. Anal. found: C, 68.87; H, 5.43; N, 7.82. Calc. for $C_{30}H_{27}N_3O_6$: C, 68.56; H, 5.18; N, 8.00.

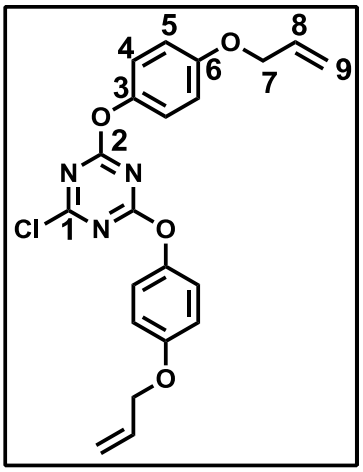


2.48

*Preparation of 2-chloro-4,6-bis(4-allyloxyphenoxy)-1,3,5-triazine (**2.48a**)*

4-Allyloxyphenol (**2.43**) (0.9 g, 6 mmol) was added dropwise to a mixture of cyanuric chloride (1.23 g, 3 mmol) and K_2CO_3 (0.83 g, 6 mmol) in acetone (50 ml) at 0°C. The mixture was stirred at this temperature for an hour followed by two hours at room temperature. Finally the mixture was refluxed for 48 hours. The mixture was cooled to room temperature and the white material was filtered off. Concentrating the filtrate *in vacuo* gave a crude white powder. Purification of the crude product by column chromatography using 5:95 (ethyl

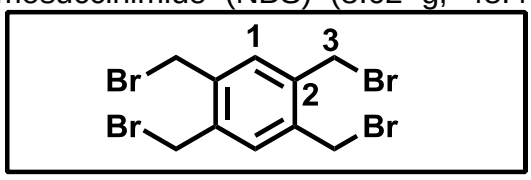
acetate:petroleum ether) solvent ratio gave pure **2.48a** as a white powder (1.5 g, 60%), m.p. 89-90^{o}C. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.56 (4H, d, J = 5.32 Hz, H7), 5.32 (2H, dd, J = 10.4, 1.3 Hz, H9), 5.43 (2H, dd, J = 17.2, 1.6 Hz, H9'), 6.02-6.09 (2H, m, H8), 6.96 (4H, d, J = 9.0 Hz, H5), 7.08 (4H, d, J = 9.0 Hz, H4). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 69.47, C7, 115.88 C5, 118.25 C9, 122.01 C4, 133.10 C8, 144.86 C3, 157.27 C6, 171.63 C1, 173.28 C2. ESI-MS: found MH^+ = 412.1063; $C_{21}H_{19}ClN_3O_4$ requires MH^+ = 412.1059. IR(cm^{-1}) 3065, 3016, 2925, 2851, 2467, 2439, 1882, 1728, 1648, 1596, 1553, 1506, 1421, 1304, 1257, 1205, 1106, 1014, 926, 874, 831, 800, 722.



2.48a

*Preparation of 1,2,4,5-tetrakis(bromomethyl)benzene (**2.52**)*

Compound **2.52** was synthesized using a literature method.[155] A mixture of durene (1.7 g, 12.7 mmol) and N-bromosuccinimide (NBS) (8.62 g, 48.4 mmol) in dry dichloromethane (40 ml) was irradiated by a 200 W lamp for 20 hours under reflux. After cooling, succinimide, which precipitated as a colourless powder, was filtered off and washed with dichloromethane. After removal of the solvent from the filtrate, the crude product was suspended in MeOH (100 ml) and stirred for 5 min to remove unreacted NBS and byproducts such as perbrominated durene. The resulting suspension was filtered and the insoluble material was washed with MeOH to give **2.52** (1.34 g, 24%) as a white solid. The spectral data were similar to those reported in the literature.[155] m.p. 123-125^{o}C (lit.m.p. 149-151^{o}C). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.60 (8H, s, H3), 7.37 (2H, s, H1).

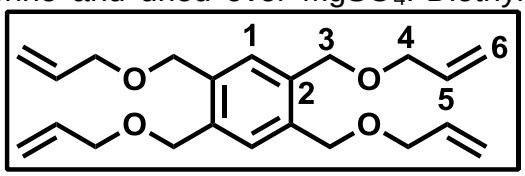


2.52

*Preparation of 1,2,4,5-tetrakis(allyloxymethyl)benzene (**2.53**)*

Allyl alcohol (0.55 ml, 8 mmol) was added dropwise to a mixture of **2.52** (0.90 g, 2 mmol) and NaH (0.19 g, 8 mmol) in dry THF (40.0 ml) at 0^{o}C. The mixture

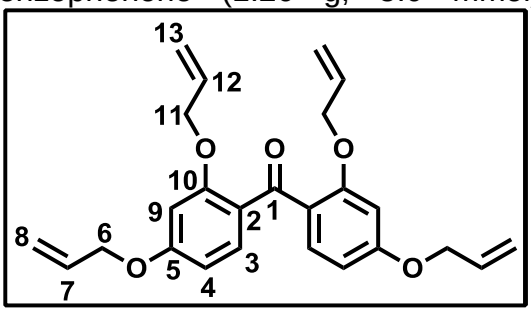
was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and NaH was quenched with 30.0 ml of 1 M aqueous NH_4Cl solution followed by 3x30 ml diethyl ether extraction. The organic layer was washed with water, brine and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give a yellow oily liquid. Purification with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **2.53** as a yellow oily liquid (0.26 g, 36.3%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.02 (8H, d, J = 5.5 Hz, H4), 4.59 (8H, s, H3), 5.20 (4H, dd, J = 10.5, 1.5 Hz, H6), 5.30 (4H, dd, J = 17.0, 1.5 Hz, H6'), 5.91-5.99 (4H, m, H5), 7.43 (2H, s, H1). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 69.71 C3, 71.45 C4, 117.37 C6, 129.73 C1, 134.98 C5, 136.15 C2. ESI-MS: found MNa^+ = 381.2039; $C_{22}H_{30}O_4Na$ requires MNa^+ = 381.2036.



2.53

*Preparation of 2,2',4,4'-tetraallyloxybenzophenone (**2.54**)*

A mixture of 2,2',4,4'-tetrahydroxybenzophenone (1.26 g, 5.0 mmol), allylbromide (1.75 ml, 20.0 mmol), K_2CO_3 (2.76 g, 20 mmol) in acetone (50 ml) was refluxed overnight. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a yellow oily liquid. The oily liquid was washed with 50 ml of 1 M NaOH solution and the organic layer was extracted with 3x40 ml diethyl ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give the crude product as a white solid material. Recrystallization from absolute alcohol gave pure **2.54** as white crystals (1.24 g, 61%), m.p. = 39-41^{o}C. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.33 (4H, d, J = 4.5 Hz, H11), 4.56 (4H, d, J = 5.0 Hz, H6), 4.95 (2H, dd, J = 17.5, 1.5 Hz, H13'), 5.01 (2H, dd, J = 10.5, 1.5 Hz, H13), 5.30 (2H, dd, J = 10.5, 1.5 Hz, H8), 5.42 (2H, dd, J = 17.5, 1.5 Hz, H8'), 5.62-5.70 (2H, m, H12), 5.99-6.06 (2H, m, H7), 6.40 (2H, s, H9), 6.52 (2H, d, J



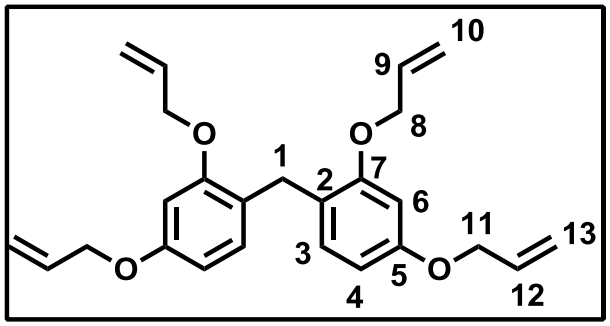
2.54

= 8.5 Hz, H4), 7.55 (2H, d, J = 8.5 Hz, H3). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 68.92 and 68.99 C6,C11, 100.14 C9, 105.67 C4, 116.54 C13, 117.99 C8, 124.70 C2, 132.21 C3, 132.37 C12, 132.78 C7, 159.01 C10, 162.32 C5, 192.91 C1. Elem. Anal. found: C, 73.79; H, 6.61. Calc. for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. ESI-MS: found MNa^+ = 429.1671; $C_{25}H_{26}O_5Na$ requires MNa^+ = 429.1672. IR (cm^{-1}): 3083, 3023, 2863, 2612, 1880, 1631, 1601, 1501, 1424, 1357, 1269, 1182, 1119, 1029, 936, 840, 815, 766.

*Preparation of bis(2,4-diallyloxyphenyl)methane (**2.59**)*

In an attempt to synthesis 1,1,2,2-tetrakis(2,4-diallyloxy)phenylethene from 2,2',4,4'-tetrahydroxybenzophenone using McMurry coupling and subsequent allylation reaction bis(2,4-diallyloxyphenyl)methane was obtained.

$TiCl_4$ (11.15 ml, 100.7 mmol) was added dropwise under nitrogen to a stirred suspension of zinc powder (14.80 g, 227 mmol) in dry THF (80 ml) at -50^{o}C. When the addition was complete, the mixture was warmed to room temperature and then refluxed for 2 hours. A solution of 2,2',4,4'-tetrahydroxybenzophenone (4.0 g, 16 mmol) in dry THF (120 ml) was added to the cooled suspension of titanium reagent at 0^{o}C and the mixture was refluxed for 2 hours. The reaction was cooled to room temperature and quenched with aqueous K_2CO_3 (30 ml), filtered through Celite, and extracted with 3x30 ml ethyl acetate. The organic layer was washed with water, brine, dried over $MgSO_4$, and concentrated *in vacuo*. Without any further purification the crude product was mixed with K_2CO_3 (6.0 g, 43.4 mmol) and allyl bromide (5.0 ml, 57.4 mmol) in acetone (80 ml) and was refluxed for two days. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a yellow oily liquid. The oily liquid was washed with 60 ml of 1.5 M NaOH solution and the organic layer was extracted with 3x50 ml diethyl

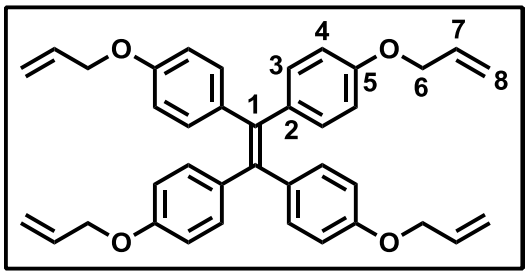


2.59

ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give a crude product. Column chromatography with 10:90 (ethyl acetate:petroleum ether) solvent ratio gave pure **2.59** as light yellow oily liquid. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 3.89 (2H, s, H1), 4.50 (8H, d, J = 5.2 Hz, H8,H11), 5.25 (2H, dd, J = 10.5, 1.5 Hz, H10,H13), 5.27 (2H, dd, J = 17.6, 1.5 Hz, H10',H13'), 5.38 (2H, dd, J = 11, 1.7 Hz, H13,H10), 5.41 (2H, dd, J = 17.3, 1.7 Hz, H13',H10'), 6.00-6.09 (4H, m, H9,H12), 6.41 (2H, d, J = 8.3 Hz, H4), 6.48 (2H, s, H6), 6.97 (2H, d, J = 8.3 Hz, H3). ^{13}C N.M.R. (126 MHz, $CDCl_3$): δ 28.85 C1, 69.02 and 69.18 C8,C11, 100.50 C6, 105.34 C4, 117.19 and 117.83 C10,C13, 122.75 C2, 130.85 C3, 133.74 and 133.75 C9,C12, 158.17 and 157.46 C5,C7. Elem. Anal. found: C, 76.78; H, 7.44. Calc. for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. ESI-MS: found MH^+ = 393.2070; $C_{25}H_{29}O_4$ requires MH^+ = 393.2060. IR (cm^{-1}): 3081, 3018, 2984, 2861, 2918, 1648, 1611, 1586, 1503, 1457, 1421, 1381, 1360, 1291, 1256, 1174, 1123, 1029, 924, 831, 778.

*Preparation of 1,1,2,2-tetrakis(4-allyloxyphenyl)ethene (**2.62**)*

Ligand **2.62** was synthesized by using a modification of two literature methods.[142, 148] $TiCl_4$ (6.2 ml, 56 mmol) was added dropwise under nitrogen to a stirred suspension of zinc powder (8.20 g, 126 mmol) in dry THF (80 ml) at -50°C. When the addition was complete, the mixture was warmed to room temperature and then refluxed for 2 hours. A solution of 4,4'-dihydroxybenzophenone (4.0 g, 18 mmol) in dry THF (120 ml) was added to the cooled suspension of titanium reagent at 0°C and the mixture was refluxed for 2 hours. The reaction was cooled to room temperature and quenched with aqueous K_2CO_3 (30 ml), filtered through Celite, and extracted with 3x30 ml ethyl acetate. The organic layer was washed with water, brine, dried over $MgSO_4$, and concentrated *in vacuo*. Without any further purification the crude product was mixed with K_2CO_3 (4.0 g, 28.9 mmol) and allyl bromide (2.0 ml, 23 mmol) in acetone (120 ml) and was refluxed overnight. The reaction

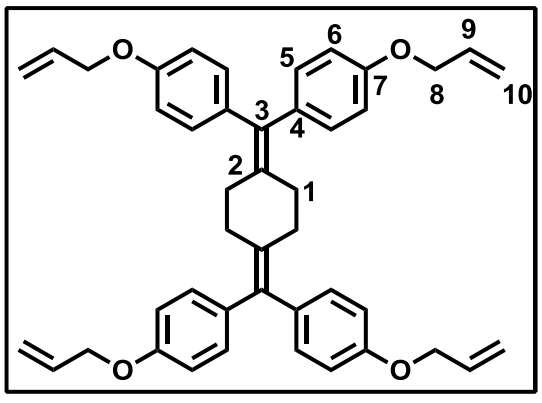


2.62

mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a yellow oily liquid. The oily liquid was washed with 60 ml of 1.5 M NaOH solution and the organic layer was extracted with 3x50 ml diethyl ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give a crude product. Column chromatography with 5:95 (ethyl acetate:petroleum ether) solvent ratio gave impure **2.62**. Recrystallization from hot ethanol gave the pure product as white needle shaped crystals (1.0 g, 31%), m.p. = 46-48^oC. ^1H N.M.R. (500MHz, $CDCl_3$): δ 4.46 (8H, bd, J = 3.0 Hz, H6), 5.26 (4H, dd, J = 10.5, 1.5 Hz, H8), 5.39 (4H, dd, J = 17.0, 1.5 Hz, H8'), 5.98-6.06 (4H, m, H7), 6.65 (8H, d, J = 8.5 Hz, H4), 6.92 (8H, bs, H3). ^{13}C N.M.R. (126 MHz, $CDCl_3$): δ 68.65 C6, 113.73 C4,C3, 117.59 C8, 132.54 C3,C4, 133.34 C7, all quaternary carbons (C1, C2, C5) not observed. Elem. Anal. found: C, 82.17; H, 6.59. Calc. for $C_{38}H_{36}O_4$: C, 81.99; H, 6.52. ESI-MS: found MH^+ = 557.2685; $C_{38}H_{37}O_4$ requires MH^+ = 557.2686. IR (cm^{-1}): 3022, 2987, 2879, 2734, 2525, 1893, 1647, 1606, 1572, 1500, 1454, 1407, 1380, 1284, 1244, 1173, 1113, 996, 928, 863, 837,800,767, 745.

*Preparation of 1,4-bis(bis(4-allyloxyphenyl)methylidene)cyclohexane (**2.65**)*

Ligand **2.65** was synthesized by using a modification of two literature methods.[142, 148] $TiCl_4$ (6.2 ml, 56 mmol) was added dropwise under nitrogen to a stirred suspension of zinc powder (8.20 g, 126 mmol) in dry THF (80 ml) at -50^oC. When the addition was complete, the mixture was warmed to room temperature and then refluxed for 2 hours. A solution of 4,4'-dihydroxybenzophenone (4.0 g, 18 mmol) and 1,4-cyclohexanedione (4.26 g, 38 mmol) in dry THF (120 ml) was added to the cooled suspension of titanium reagent at 0^oC and the mixture was refluxed for 2 hours. The reaction was cooled to room temperature and quenched with aqueous K_2CO_3 (30 ml), filtered through Celite, and extracted with 3x30 ml ethyl acetate. The organic

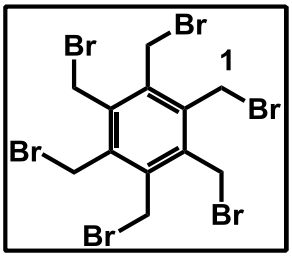


2.65

layer was washed with water, brine, dried over $MgSO_4$, and concentrated *in vacuo*. Without any further purification the crude product was mixed with K_2CO_3 (6.0 g, 43.4 mmol) and allyl bromide (5.0 ml, 57.4 mmol) in acetone (80 ml) and was refluxed for two days. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a yellow oily liquid. The oily liquid was washed with 60 ml of 1.5 M NaOH solution and the organic layer was extracted with 3x50 ml diethyl ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give a crude product. Column chromatography with 10:90 (ethyl acetate:petroleum ether) solvent ratio gave crude **2.65**. Recrystallization from hot ethanol gave the pure product as a white fluffy material, m.p. = 74-76^oC. ^1H N.M.R. (500MHz, $CDCl_3$): δ 2.37 (8H, s, H1), 4.50 (8H, d, J = 5.5 Hz, H8), 5.27 (4H, dd, J = 10.5, 1.5 Hz, H10), 5.40 (4H, dd, J = 17.0, 1.5 Hz, H10'), 5.99-6.06 (4H, m, H9), 6.80 (8H, d, J = 8.5 Hz, H6), 7.02 (8H, d, J = 9.0 Hz, H5). ^{13}C N.M.R. (126 MHz, $CDCl_3$): δ 33.56 C1, 114.25 C6, 117.86 C10, 131.13 C5, 133.66 C9, 134.72 C3, 136.01 C4, 137.13 C2, 157.26 C7. Elem. Anal. found: C, 82.92; H, 6.92. Calc. for $C_{44}H_{44}O_4$: C, 82.99; H, 6.96. ESI-MS: found MH^+ = 637.3312; $C_{44}H_{45}O_4$ requires MH^+ = 637.3310. IR (cm^{-1}): 3085, 3041, 2982, 2882, 2841, 1865, 1645, 1605, 1572, 1500, 1462, 1424, 1363, 1281, 1228, 1175, 1110, 1022, 990, 916, 842, 810, 746.

*Preparation of hexakis(bromomethyl)benzene (**2.67**)*

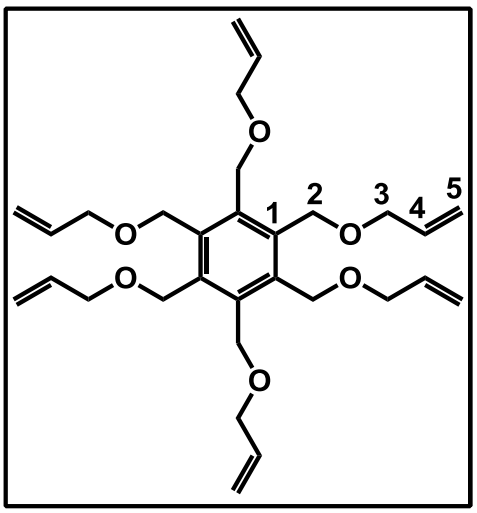
A literature method was adopted to synthesize **2.67**.[159] A mixture of hexamethylbenzene (6.5 g, 0.04 mol) and ethylenebromide (180 ml, 2.08 mol) was stirred under reflux until all hexamethylbenzene dissolved. Bromine (20 ml, 0.39 mol) was added portionwise to this solution which was then refluxed for 18 hours. Upon cooling white crystals formed which were collected by filtration to give **2.67** as a white crystalline material (23.25 g, 92%), m.p. 288-290^oC (lit. 297^oC [159]). ^1H N.M.R. (300MHZ, $CDCl_3$): δ 4.70 (s, H1) which matches the literature value.[159]



2.67

*Preparation of hexakis(allyloxymethyl)benzene (**2.68**)*

Allyl alcohol (0.23 ml, 3.3 mmol) was added dropwise to a mixture of **2.67** (1.91 g, 3.0 mmol) and NaH (0.08 g, 3.3 mmol) in dry THF (30.0 ml) at 0^{o}C. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 30.0 ml of 1 M aqueous NH_4Cl solution followed by 3x30 ml diethyl ether extraction. The organic layer was washed with water, brine and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give a yellow oily liquid. Purification with silica gel column chromatography using 20:80 (ethyl acetate:petroleum ether) solvent ratio gave **2.68** as a yellow oily liquid (1.26 g, 80.3%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.05 (12H, d, J = 5.7 Hz, H3), 4.65 (12H, s, H2), 5.20 (6H, dd, J = 10.3, 1.7 Hz, H5), 5.30 (6H, dd, J = 17.3, 1.7 Hz, H5'), 5.92-5.99 (6H, m, H4). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 65.90 C2, 71.84 C3, 117.53 C5, 135.10 C4, 138.13 C1. Elem. Anal. found: C, 71.99; H, 8.38. Calc. for $C_{30}H_{42}O_6$: C, 72.26; H, 8.49. ESI-MS: found MH^+ = 499.3059; $C_{30}H_{43}O_6$ requires MH^+ = 499.3054. IR (cm^{-1}) 2850, 1995, 1856, 1726, 1646, 1511, 1450, 1421, 1341, 1129, 1079, 925.



2.68

6.1.3 General procedure for the preparation of ligands containing diallylamine group

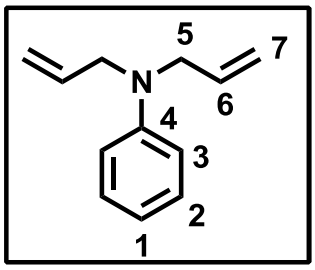
Two different literature procedures were used for the synthesis of ligands containing diallylamine group. For those ligands synthesized from the combination of an aryl amine with allylbromide, Huang's[151] method was used. Two equivalents of allylbromide were added to a mixture of one equivalent of the corresponding amine and NaH in 60 ml of dry THF. The resulting solution was refluxed for three days and quenched with 10% ammonium chloride solution. The organic layer was extracted with 3x75 ml of diethyl ether and

washed with water and brine solutions, respectively. The resulting solution was dried over $MgSO_4$ followed by removal of the solvent under vacuum. Finally the target material was purified by column chromatography using silica gel (60 mesh, 200-300) and different ethyl acetate / petroleum ether solvent ratios.

For those ligands synthesized from the combination of haloarenes and N,N-diallylamine Reedijk's[152] procedure was used. One equivalent of diallylamine was added to a mixture of one equivalent of haloarene and N,N-diisopropylethylamine (DIPEA) in 80 ml of dry acetonitrile at 0^oC. The resulting solution was stirred for an hour at this temperature followed by 2 hours at room temperature. Finally the solution was refluxed for 48 hours. The reaction mixture was cooled to room temperature, which resulted in a white crystalline material. The crystalline material was filtered off and the solution concentrated *in vacuo* which resulted in a yellow oily liquid. The oily liquid was dissolved in diethyl ether and washed with water, brine and finally dried over $MgSO_4$ followed by removal of the solvent under vacuum. The target material was purified by column chromatography using silica gel (60 mesh, 200-300) and different ethyl acetate / petroleum ether solvent ratios.

*Preparation of N,N-diallylaminobenzene (**3.12**)*

Ligand **3.12** was synthesized by using a literature method.[151] A mixture of aniline (0.46 ml, 5 mmol) and NaH (0.25 g, 10.5 mmol) was stirred in dry THF (50 ml) at 0^oC. Allylbromide (0.91 ml, 10.5 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 50 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x30 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave a dark red oily liquid. Purification of the crude product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum

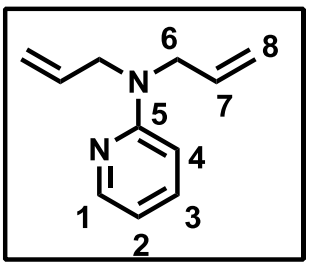


3.12

ether) solvent ratio gave **3.12** as a yellow oily liquid (0.84 g, 97%). The spectral data were similar with those reported in the literature.[151, 230] ^{1}H N.M.R. (300MHZ, $CDCl_3$): δ 3.95 (4H, d, J = 4.8 Hz, H5), 5.14-5.21 (4H, m, H7), 5.82-5-94 (2H, m, H6), 6.62 (1H, t, J = 7.2 Hz, H1), 6.69 (2H, d, J = 9.0 Hz, H3), 7.16 (2H, dd, J = 9.0,7.2 Hz, H2). ^{13}C N.M.R. (75MHz): δ 52.85 C5, 112.45 C3, 116.04 C7, 116.38 C1, 129.17 C2, 134.17 C6, 148.83 C4. ESI-MS: found MH^+ = 174.1277; $C_{12}H_{16}N$ requires MH^+ = 174.1277. IR (cm^{-1}) 3090, 3056, 2956, 1690, 1643, 1599, 1505, 1232, 1181, 989, 919, 745.

*Preparation of 2-(N,N-diallylamino)pyridine (**3.13**)*

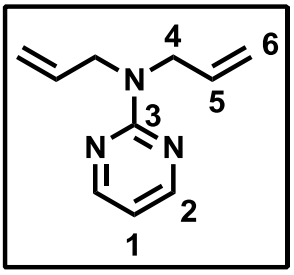
A mixture of 2-aminopyridine (1.88 g, 20 mmol) and NaH (0.96 g, 40 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (3.48 ml, 40 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 50 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x30 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave a dark red oily liquid. Purification of the crude product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **3.13** as a yellow oily liquid (3.20 g, 92%). The spectral data were similar with those reported in the literature.[231-232] ^{1}H N.M.R. (300MHZ, $CDCl_3$): δ 4.11 (4H, d, J = 5.0 Hz, H6), 5.12-5.17 (4H, m, H8), 5.82-5.90 (2H, m, H7), 6.46 (1H, d, J = 8.5 Hz, H4), 6.52 (1H, dd, J = 6.5, 5.5 Hz, H2), 7.39 (1H, dd, J = 8.5, 7.5 Hz, H3), 8.15 (1H, d, J = 6.0 Hz, H1). ^{13}C N.M.R. (126MHz): δ 50.04 C6, 106.04 C4, 111.78 C2, 115.99 C8, 133.96 C7, 137.11 C3, 147.88 C1, 157.97 C5. ESI-MS: found MH^+ = 175.1229; $C_{11}H_{15}N_2$ requires MH^+ = 175.1230. IR (cm^{-1}) 3076, 3008, 2918, 2980, 2524, 2376, 2266, 1931, 1846, 1722, 1641, 1595, 1560, 1491, 1436, 1416, 1391, 1359, 1317, 1279, 1244, 1186, 1160, 1130, 1094, 1070, 1055, 1023, 993, 978, 919, 768, 732.



3.13

*Preparation of 2-(N,N-diallylamino)pyrimidine (**3.14**)*

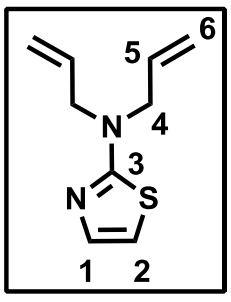
A mixture of 2-aminopyrimidine (1.90 g, 20 mmol) and NaH (0.96 g, 40 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (3.48 ml, 40 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 50 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x30 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave a dark red oily liquid. Purification of the crude product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **3.14** as a yellow oily liquid (1.61 g, 46%). ^{1}H N.M.R. (300MHZ, $CDCl_3$): δ 4.21 (4H, d, J = 5.4 Hz, H4), 5.09-5.15 (4H, m, H6), 5.78-5.91 (2H, m, H5), 6.44 (1H, t, J = 4.8 Hz, H1), 8.29 (2H, d, J = 4.8 Hz, H2). ^{13}C N.M.R. (75MHz): δ 49.00 C4, 109.81 C1, 116.32 C6, 134.06 C5, 158.05 C2, 161.72 C3. ESI-MS: found MH^+ = 176.1179; $C_{10}H_{14}N_3$ requires MH^+ = 176.1182. IR (cm^{-1}) 3078, 3027, 2982, 2924, 2854, 1848, 1766, 1641, 1585, 1547, 1505, 1414, 1387, 1361, 1346, 1315, 1268, 1221, 1180, 1084, 1031, 994, 980, 920, 798, 780, 688.



3.14

*Preparation of 2-(N,N-diallylamino)thiazole (**3.15**)*

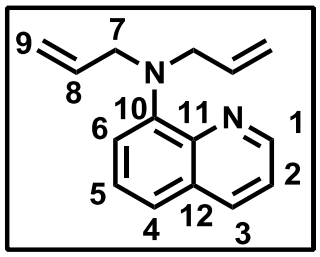
A mixture of 2-aminothiazole (0.50 g, 5 mmol) and NaH (0.48 g, 20 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (0.87 ml, 10 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for 36 hours. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x20 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave a dark red oily liquid. Purification of the crude product with silica gel



3.15

column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **3.15** as a light yellow oily liquid (0.74 g, 82%). ^{1}H N.M.R. (300MHZ, $CDCl_3$): δ 4.06 (4H, d, J = 5.7 Hz, H4), 5.18-5.24 (4H, m, H6), 5.79-5.89 (2H, m, H5), 6.46 (1H, d, J = 3.6 Hz, H2), 7.15 (1H, d, J = 3.6 Hz, H1). ^{13}C N.M.R. (126MHz): δ 53.26 C4, 106.55 C2, 117.96 C6, 132.60 C5, 139.60 C1, quaternary carbon C3 not observed. ESI-MS: found MNa^+ = 203.0622; $C_9H_{12}N_2SNa$ requires MNa^+ = 203.0613. IR (cm^{-1}) 3475, 3079, 2923, 1717, 1641, 1531, 1417, 1364, 1310, 1225, 1198, 1126, 1055, 992, 925, 749.

*Preparation of 8-diallylaminoquinoline (**3.16**)*

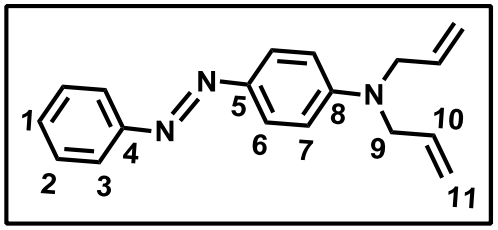


3.16

A mixture of 8-aminoquinoline (0.72 g, 5 mmol) and NaH (0.24 g, 10 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (0.87 ml, 10 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 50 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x50 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave a dark red oily liquid. Purification of the crude product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **3.16** as a yellow oily liquid (0.99 g, 88%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.16 (4H, d, J = 6.3 Hz, H7), 5.13 (2H, dd, J = 10.3, 1.4 Hz, H9), 5.18 (2H, dd, J = 17.5, 1.4 Hz, H9'), 5.86- 6.00 (2H, m, H8), 7.10 (1H, dd, J = 6.5, 2.5 Hz, H6), 7.32-7.40 (3H, m, H2, H4, H5), 8.08 (1H, dd, J = 8.4, 1.8 Hz, H3), 8.89 (1H, dd, J = 4.2, 1.8 Hz, H1). ^{13}C N.M.R. (126MHz): δ 55.80 C7, 117.67 C9, 118.78 C4, 121.04 C6, 121.12 C5, 126.53 C2, 129.99 C12, 135.43 C8, 136.70 C3, 143.29 C11, 147.59 C10, 148.11 C1. ESI-MS: found MNa^+ = 247.1218; $C_{15}H_{16}N_2Na$ requires MNa^+ = 247.1206. IR (cm^{-1}) 3073, 2977, 1841, 1662, 1640, 1607, 1595, 1566, 1499, 1470, 1390, 1242, 1100, 918, 791.

*Preparation of 4-(N,N-diallylamino)azobenzene (**3.17**)*

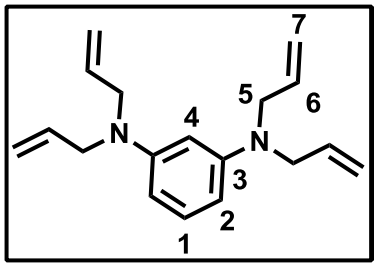
A mixture of 4-aminoazobenzene (1.97 g, 10 mmol) and NaH (0.48 g, 20 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (1.74 ml, 20 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 50 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x50 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure red oily liquid. Purification of the crude product with silica gel column chromatography using petroleum ether solvent gave **3.17** as a red oily liquid (1.8 g, 65%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.02 (4H, d, J = 4.5 Hz, H9), 5.17-5.22 (4H, m, H11), 5.84-5.92 (2H, m, H10), 6.76 (2H, d, J = 9.0 Hz, H7), 7.38 (2H, dd, J = 7.0, 7.5 Hz, H2), 7.47 (1H, t, J = 8.0 Hz, H1), 7.83-7.86 (4H, m, H3,H6). ^{13}C N.M.R. (126MHz): δ 53.05 C9, 112.00 C7, 116.70 C11, 122.44 C3, 125.21 C6, 129.17 C2, 129.63 C1, 133.13 C10, 144.11 C5, 151.32 C8, 153.47 C4. ESI-MS: found MNa^+ = 300.1473; $C_{18}H_{19}N_3Na$ requires MNa^+ = 300.1471. IR (cm^{-1}) 3081, 3008, 2980, 2909, 2642, 1700, 1642, 1600, 1566, 1513, 1461, 1448, 1435, 1414, 1392, 1356, 1334, 1313, 1236, 1177, 1155, 1140, 1069, 1019, 990, 921, 821, 767, 723, 689.



3.17

*Preparation of N^1,N^1,N^3,N^3-tetraallyl-1,3-diaminobenzene (**3.24**)*

A mixture of 1,3-phenylenediamine (1.5 g, 13.8 mmol) and NaH (1.33 g, 55.4 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (4.83 ml, 55.5 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for a week. The reaction was cooled to room temperature and NaH was quenched with 50 ml of 1M

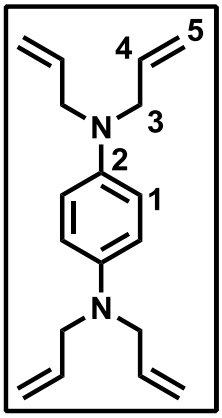


3.24

aqueous NH_4Cl solution. The organic layer was extracted with 3x50 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure yellow oily liquid. Purification of the crude product with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **3.24** as a light yellow oily liquid (1.98 g, 53%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 3.91(8H, d, J = 5.0 Hz, H5), 5.16 (4H, dd, J = 10.0, 1.5 Hz, H7), 5.21 (4H, dd, J = 17.0, 1.5 Hz, H7'), 5.84-5.91 (4H, m, H6), 6.10-6.14 (3H, m, H2,H4), 7.05 (1H, t, 8.0 Hz, H1). ^{13}C N.M.R. (126MHz): δ 53.25 C5, 97.44 C4, 101.95 C2, 116.12 C7, 129.75 C1, 134.87 C6, 150.14 C3. ESI-MS: found MH^+ = 269.2018; $C_{18}H_{25}N_2$ requires MH^+ = 269.2012. IR (cm^{-1}) 3077, 3005, 2924, 2853, 1838, 1641, 1603, 1571, 1505, 1459, 1416, 1357, 1335, 1288, 1248, 1205, 1179, 1128, 1042, 991, 960, 916, 809, 744, 687.

*Preparation of N^1,N^1,N^4,N^4-tetraallyl-1,4-diaminobenzene (**3.25**)*

A mixture of 1,4-phenylenediamine (0.54 g, 5 mmol) and NaH (0.49 g, 20.5 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (1.8 ml, 20.5 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x30 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure dark brown oily liquid. Purification of the crude product with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **3.25** as a light yellow oily liquid (2.0 g, 78%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 3.83 (8H, d, J = 3.9 Hz, H3), 5.14 (4H, dd, J = 10.2, 1.5 Hz, H5), 5.20 (4H, dd, J = 17.4, 1.5 Hz, H5'), 5.80-5.91 (4H, m, H4), 6.70 (4H, s, H1). ^{13}C N.M.R. (75MHz, $CDCl_3$): δ 54.06 C3, 115.42 C1, 116.43 C5, 135.19 C4, 142.00 C2. ESI-MS: found MNa^+ = 291.1838; $C_{18}H_{24}N_2Na$ requires MNa^+ =

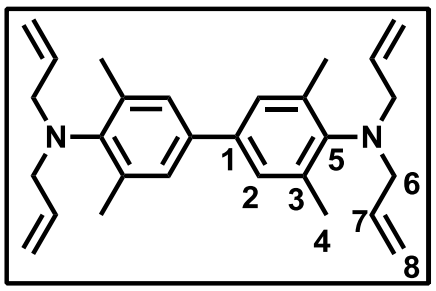


3.25

291.1832. IR (cm $^{-1}$) 3077, 3005, 2977, 2912, 1842, 1641, 1612, 1517, 1417, 1356, 1333, 1285, 1231, 1182, 1068, 992, 917, 805, 725.

*Preparation of $N^4,N^4,N^{4'},N^{4'}$-tetraallyl-4,4'-diamino-3,3',5,5'-tetramethylbiphenyl (**3.26**)*

A mixture of 3,3',5,5'-tetramethylbiphenyl-4,4'-diamine (1.20 g, 5 mmol) and NaH (0.49 g, 20.5 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (1.8 ml, 20.5 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x30 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure dark brown oily liquid. Purification of the crude product with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **3.26** as a light yellow oily liquid that solidified on standing. Recrystallisation from acetone gave colourless crystals suitable for X-ray crystallography analysis (1.0 g, 50%), m.p. (54-56^{o}C). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 2.34 (12H, s, H4), 3.65 (8H, d, J = 6.3 Hz, H6), 5.04 (4H, d, J = 9.9 Hz, H8), 5.13 (4H, d, J = 15.9 Hz, H8'), 5.78-5.92 (4H, m, H7), 7.18 (4H, s, H2). ^{13}C N.M.R. (75MHz, $CDCl_3$): δ 20.14 C4, 56.17 C6, 116.34 C8, 127.50 C2, 137.16 C3, 137.66 C7, 147.48 C5, C1 not observed. Elem. Anal. found: C, 84.38; H, 9.29; N, 6.90. Calc. for $C_{28}H_{36}N_2$: C, 83.95; H, 9.06; N, 6.99. ESI-MS: found MH^+ = 401.2938; $C_{28}H_{37}N_2$ requires MH^+ = 401.2951. IR (cm^{-1}) 3071, 2976, 2923, 2824, 1829, 1676, 1640, 1604, 1473, 1434, 1418, 1369, 1267, 1206, 1166, 1100, 1031, 991, 914, 861, 799, 653.

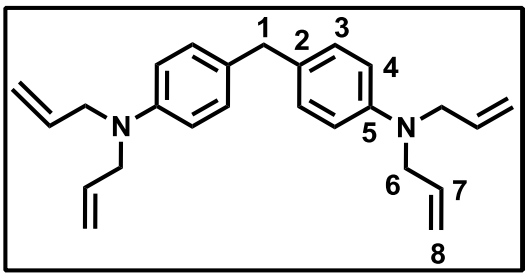


3.26

*Preparation of $N^4,N^4,N^{4'},N^{4'}$-tetraallyl-4,4'-diaminodiphenylmethane (**3.27**)*

A mixture of 4,4'-diaminodiphenylmethane (0.99 g, 5 mmol) and NaH (0.49 g, 20.5 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (1.8 ml, 20.5

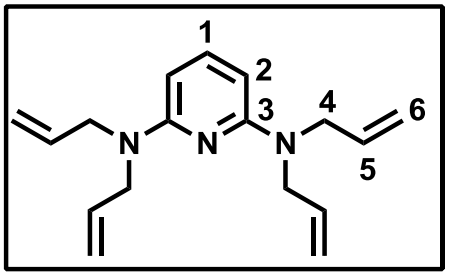
mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x30 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure dark brown oily liquid. Purification of the crude product with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **3.27** as a light yellow oily liquid (1.31 g, 73%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 3.77 (2H, s, H1), 3.89 (8H, d, J = 4.5 Hz, H6), 5.15 (4H, dd, J = 10.0, 1.5 Hz, H8), 5.18 (4H, dd, J = 17.0, 1.5 Hz, H8'), 5.80-5.92 (4H, m, H7), 6.64 (4H, d, J = 9.0 Hz, H4), 7.02 (4H, d, J = 8.5 Hz, H3). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 40.07 C1, 53.10 C6, 112.74 C4, 116.16 C8, 129.60 C3, 130.06 C2, 134.54 C7, 147.17 C5. ESI-MS: found MH^+ = 359.2499; $C_{25}H_{31}N_2$ requires MH^+ = 359.2482. IR(cm^{-1}) 3078, 3007, 2978, 2923, 2853, 1847, 1680, 1641, 1613, 1567, 1516, 1439, 1417, 1387, 1357, 1336, 1286, 1231, 1187, 1131, 1066, 1044, 991, 917, 797, 753.



3.27

*Preparation of N^2,N^2,N^6,N^6-tetraallyl-2,6-diaminopyridine (**3.28**)*

A mixture of 2,6-diaminopyridine(1.09 g, 10 mmol) and NaH (0.96 g, 40 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (3.48 ml, 40 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x40 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure dark brown oily liquid. Purification of the crude

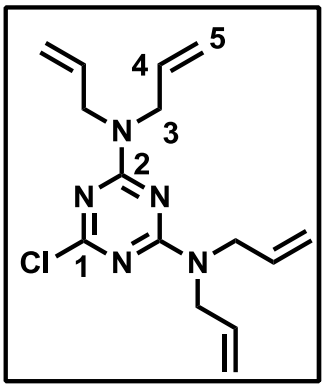


3.28

product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **3.28** as a red oily liquid (2.40 g, 94%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.06 (8H, d, J = 5.4 Hz, H4), 5.11 (4H, dd, J = 10.5, 1.5 Hz, H6), 5.16 (4H, dd, J = 17.4, 1.5 Hz, H6'), 5.78 (2H, d, J = 8.1 Hz, H2), 5.81-5.93 (4H, m, H5), 7.23 (1H, t, J = 8.1 Hz, H1). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 50.37 C4, 93.55 C2, 115.90 C6, 135.13 C5, 138.83 C1, C3 not observed. ESI-MS: found MH^+ = 270.1969; $C_{17}H_{24}N_3$ requires MH^+ = 270.1965. IR (cm^{-1}) 3078, 2926, 2853, 1840, 1640, 1584, 1476, 1414, 1402, 1376, 1358, 1341, 1260, 1228, 1201, 1183, 1164, 1052, 993, 936, 916, 768, 712.

*Preparation of 2,4-bis(diallylamino)-6-chloro-1,3,5-triazine (**3.29**)*

A mixture of cyanuric chloride (1.84 g, 10 mmol) and N,N-diisopropylethylamine (DIPEA) (3.3 ml, 20 mmol) was stirred in dry THF (60 ml) at 0^{o}C. Diallylamine (2.5 ml, 20 mmol) was added to this solution and stirred for 2 hours at this temperature. The solution was then stirred at room temperature for 2 hours and then refluxed for 48 hours. The reaction was cooled to room temperature and the crystalline salt of DIPEA filtered off using a glass sintered filter funnel. Concentrating the solution *in vacuo* gave a brown oily liquid.

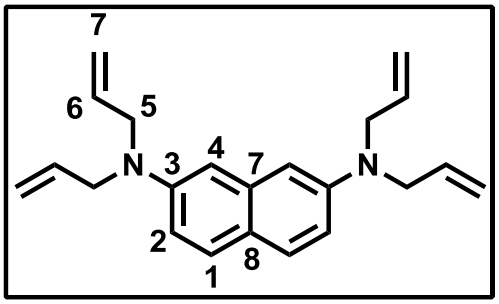


3.29

Purification of the crude product with silica gel column chromatography using petroleum ether gave **3.29** as a light yellow oily liquid (2.20 g, 72%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.10 (4H, d, J = 5.7 Hz, H3), 4.17 (4H, d, J = 5.7 Hz, H3), 5.10-5.17 (8H, m, H5), 5.72-5.85 (4H, m, H4). ^{13}C N.M.R. (75MHz, $CDCl_3$): δ 48.74, 48.85 C3, 117.33, 117.50 C5, 133.19, 133.57 C4, 165.06 C2, 169.73 C1. ESI-MS: found MNa^+ = 328.1307; $C_{15}H_{20}ClN_5Na$ requires MNa^+ = 328.1299. IR (cm^{-1}) 3080, 3010, 2924, 2855, 2526, 2326, 1850, 1642, 1563, 1494, 1414, 1314, 1254, 1237, 1195, 1171, 1110, 1044, 993, 969, 923, 850, 802, 737, 686.

*Preparation of N^2,N^2,N^7,N^7-tetraallyl-2,7-diaminonaphthalene (**3.30**)*

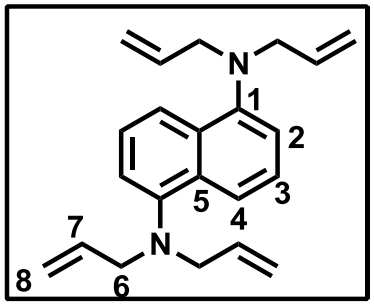
A mixture of 2,7-diaminonaphthalene (1.58 g, 10 mmol) and NaH (0.96 g, 40 mmol) was stirred in dry THF (50 ml) at 0°C. Allylbromide (3.48 ml, 40 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x40 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure dark brown oily liquid. Purification of the crude product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **3.30** as a red oily liquid (1.43 g, 45%). ^{1}H N.M.R. (300MHz, DMSO): δ 4.01 (8H, d, J = 4.8 Hz, H5), 5.16-5.24 (8H, m, H7), 5.86-5.98 (4H, m, H6), 6.68 (2H, s, H4), 6.81 (2H, d, J = 9.0 Hz, H2), 7.48 (2H, d, J = 9.0 Hz, H1). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 52.79 C5, 104.69 C4, 112.40 C2, 116.06 C7, 128.35 C1, 134.26 C6, 147.14 C3, C7 and C8 not observed. ESI-MS: found MH^+ = 319.2180; $C_{22}H_{27}N_2$ requires MH^+ = 319.2169. IR (cm^{-1}) 3079, 3006, 2978, 2907, 1842, 1738, 1624, 1518, 1475, 1430, 1399, 1358, 1288, 1251, 1217, 1194, 1129, 1022, 991, 951, 917, 846, 813, 748.



3.30

*Preparation of N^1,N^1,N^5,N^5-tetraallyl-1,5-diaminonaphthalene (**3.31**)*

A mixture of 1,5-diaminonaphthalene (1.58 g, 10 mmol) and NaH (0.96 g, 40 mmol) was stirred in dry THF (50 ml) at 0°C. Allylbromide (3.48 ml, 40 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for three days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x40 ml

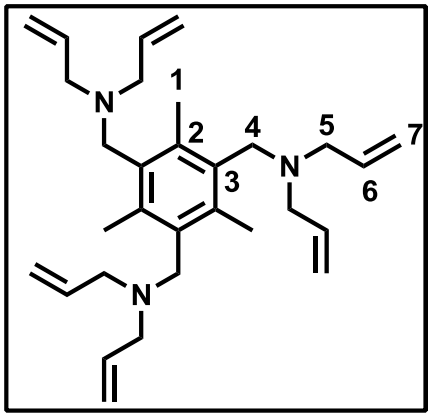


3.31

of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure dark brown oily liquid. Purification of the crude product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **3.31** as a red oily liquid (1.73 g, 70%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 3.79 (8H, d, J = 6.0 Hz, C6), 5.15 (4H, dd, 10.2, 1.5 Hz, H8), 5.25 (4H, dd, 17.1, 1.5 Hz, H8'), 5.82-5.95 (4H, m, H7), 7.08 (2H, d, J = 7.5 Hz, H2), 7.39 (2H, dd, J = 7.5, 8.1 Hz, H3), 8.04 (2H, d, J = 8.4 Hz, H4). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 56.28 C6, 117.10 C8, 117.60 C2, 119.27 C4, 124.70 C3, 131.58 C5, 135.22 C7, 148.06 C1. ESI-MS: found MH^+ = 319.2168; $C_{22}H_{27}N_2$ requires MH^+ = 319.2169. IR (cm^{-1}) 3075, 3007, 2978, 2923, 2814, 1847, 1642, 1588, 1505, 1436, 1409, 1357, 1239, 1203, 1174, 1145, 1105, 1034, 992, 919,785.

*Preparation of N^1,N^1,N^3,N^3,N^5,N^5-hexaallyl-1,3,5-triaminomethyl-2,4,6-trimethylbenzene (**3.34**)*

Diallylamine (0.74 ml, 6 mmol) was added to a mixture of **2.41** (0.80 g, 2 mmol) and KOH (0.34 g, 6 mmol) in acetone (50.0 ml) at room temperature. The mixture was refluxed for two days. The reaction was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* followed by 3x30 ml diethyl ether extraction. The organic layer was washed with water, brine and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give a yellow oily liquid. Purification with silica gel column chromatography using 10:90 (ethyl acetate:petroleum ether) solvent ratio gave **3.34** as a yellow oily liquid (0.53 g, 59%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 2.40 (9H, s, H1), 3.00 (12H, d, J = 6.5 Hz, H5), 3.60 (6H, s, H4), 5.06 (6H, d, J = 10.5 Hz, H7), 5.13 (6H, d, J = 17.5 Hz, H7'), 5.76-5.85 (6H, m, H6). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 17.10 C1, 52.80 C4, 56.55 C5, 117.02 C7, 133.39 C2,C3, 136.94 C6, 137.78 C3,C2. ESI-MS: found MNa^+ = 470.3507; $C_{30}H_{45}N_3Na$ requires MNa^+ = 470.3506.

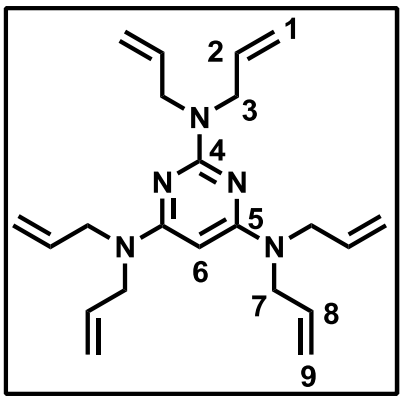


3.34

IR(cm^{-1}) 3076, 3006, 2976, 2923, 2866, 2787, 2757, 1840, 1676, 1642, 1579, 1443, 1417, 1361, 1256, 1173, 1145, 1118, 1061, 1030, 995, 976, 916, 863.

*Preparation of 2,4,6-tris(diallylamino)pyrimidine (**3.35**)*

A mixture of 2,4,6-triaminopyrimidine (0.63 g, 5 mmol) and NaH (0.72 g, 30 mmol) was stirred in dry THF (50 ml) at 0°C. Allylbromide (2.61 ml, 30 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for a week. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x30 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure yellow oily liquid. Purification of the crude product with silica gel column chromatography using 5:95 (ethyl acetate:petroleum ether) solvent ratio gave **3.35** as a light yellow oily liquid (1.78 g, 97%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.01 (8H, d, J = 5.4 Hz, H7), 4.17 (4H, d, J = 6.0 Hz, H3), 4.94 (1H, s, H6), 5.06-5.16 (12H, m, H1,H9), 5.77-5.95 (6H, m, H2,H8). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 49.21 C3, 50.10 C7, 72.27 C6, 115.77 C1, 116.21 C9, 134.92 C8, 136.11 C2, 160.76 C4, 163.55 C5. ESI-MS: found MH^+ = 366.2662; $C_{22}H_{32}N_5$ requires MH^+ = 366.2658. IR (cm^{-1}) 3077, 3004, 2952, 2924, 2854, 1836, 1640, 1563, 1468, 1408, 1376, 1340, 1317, 1286, 1265, 1210, 1144, 1113, 994, 963, 916, 787.

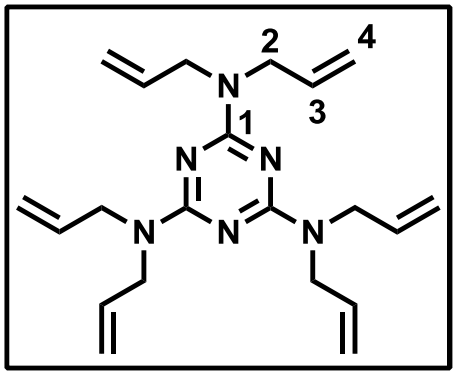


3.35

*Preparation of 2,4,6-tris(diallylamino)-1,3,5-triazine (**3.36**)*

A mixture of cyanuric chloride (0.92 g, 5 mmol) and N,N-diisopropylethylamine (DIPEA) (2.48 ml, 15 mmol) was stirred in dry THF(60 ml) at 0°C. Diallylamine (1.85 ml, 15 mmol) was added to this solution and stirred for 2 hours at this temperature. The solution was then stirred at room temperature for 2 hours and then refluxed for 48 hours. The reaction was cooled to room temperature and the crystalline salt of DIPEA filtered off using a glass sintered filter funnel.

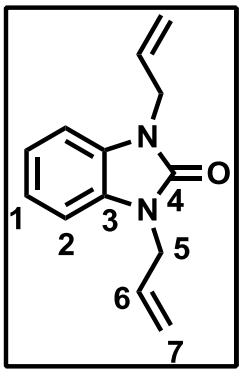
Concentrating the solution *in vacuo* gave a brown oily liquid. Purification of the crude product with silica gel column chromatography using petroleum ether gave **3.36** as a light yellow oily liquid (0.52 g, 28%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.13 (12H, d, J = 5.9 Hz, H2), 5.09 (6H, dd, J = 10.2, 1.6 Hz, H4), 5.15 (6H, dd, J = 17.1, 1.6 Hz, H4'), 5.78-5.91 (6H, m, H3). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 48.58 C2, 116.35 C4, 135.15 C3, 165.58 C1. ESI-MS: found MNa^+ = 389.2427; $C_{21}H_{30}N_6Na$ requires MNa^+ = 389.2424. IR (cm^{-1}) 3077, 2980, 2919, 1839, 1640, 1538, 1483, 1411, 1315, 1266, 1199, 995, 918, 808.



3.36

*Preparation of 1,3-diallylbenzimidazol-2-one (**4.13**)*

A mixture of 2-hydroxybenzimidazole (2.68 g, 20.0 mmol), allylbromide (3.5 ml, 40.0 mmol), K_2CO_3 (5.52 g, 40 mmol) in acetone (50 ml) was refluxed overnight. The reaction mixture was cooled to room temperature and the solid material was filtered off. The solvent was removed *in vacuo* to give a yellow oily liquid. The oily liquid was washed with 50 ml of 1 M NaOH solution and the organic layer was extracted with 3x40 ml diethyl ether. The organic extracts were combined and dried over $MgSO_4$. Diethyl ether was evaporated under reduced pressure to give the crude product as a light yellow oily liquid. Purification of the crude product with silica gel column chromatography using 20:80 (ethyl acetate:petroleum ether) solvent ratio gave pure **4.13** as a light oily liquid (3.0 g, 70%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.53 (4H, d, J = 5.0 Hz, H5), 5.20-5.24 (4H, m, H7), 5.87-5.94 (2H, m, H6), 6.99 (2H, d, J = 9.0 Hz, H1), 7.07 (2H, d, J = 9.0 Hz, H2). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 43.79 C5, 108.48 C2, 117.79 C7, 121.47 C1, 129.56 C3, 132.29 C6, 154.02 C4. ESI-MS: found MNa^+ = 237.1001; $C_{13}H_{14}N_2ONa$ requires MNa^+ = 237.0998. IR(cm^{-1}) 3489, 3064, 3014, 2985, 2918, 1863,

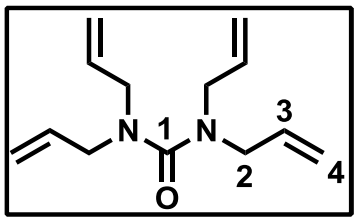


4.13

1710, 1645, 1619, 1493, 1439, 1403, 1349, 1327, 1301, 1274, 1198, 1173, 1135, 1077, 1022, 990, 926, 830, 755, 735, 692.

*Preparation of 1,1,3,3-tetraallylurea (**4.16**)*

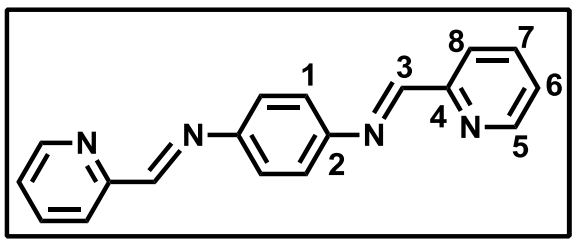
A mixture of 1,3-diallylurea(0.70 g, 5 mmol) and NaH (0.48 g, 20 mmol) was stirred in dry THF (50 ml) at 0^{o}C. Allylbromide (0.91 ml, 10.5 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x40 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure white oily liquid. Purification of the crude product with silica gel column chromatography using 30:70 (ethyl acetate:petroleum ether) solvent ratio gave **4.16** as a red brown oily liquid (0.69 g, 63%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 3.71 (8H, d, J = 5.7 Hz, H2), 5.10-5.16 (8H, m, H4), 5.72-5.83 (4H, m, H3). ^{13}C N.M.R. (75MHz, $CDCl_3$): δ 50.40 C2, 117.31 C4, 134.22 C3, 164.66 C1. ESI-MS: found MH^+ = 221.1645; $C_{13}H_{21}N_2O$ requires MH^+ = 221.1648. IR(cm^{-1}) 3079, 3009, 2982, 2927, 2860, 1847, 1738, 1643, 1462, 1433, 1404, 1360, 1278, 1230, 1196, 1132, 1048, 994, 921, 771, 732.



4.16

*Preparation of N^1,N^4-bis(2-pyridinylmethylidene)-1,4-diaminobenzene (**4.20**)*

Compound **4.20** was synthesised using a literature method.[222] A mixture of 1,4-diaminobenzene (2.16 g, 20 mmol) and 2-pyridinecarboxaldehyde (3.82 ml, 40 mmol) was refluxed in ethanol (40 ml) for 16 hours. Upon cooling yellow crystals formed which were collected by filtration to give **4.20** as a yellow crystalline material (5.21 g, 91%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 7.37-7.40 (6H, m, H1,H6), 7.83 (2H, td, J = 8.0 Hz, H7),

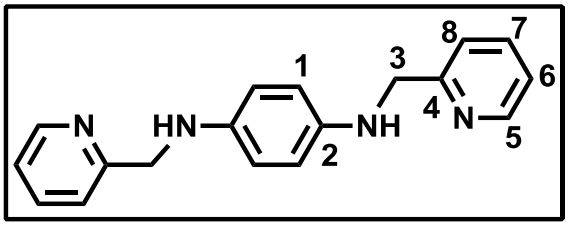


4.20

8.22 (2H, d, J = 8.0 Hz, H8), 8.66 (2H, s, H3), 8.73 (2H, d, J = 5.0 Hz, H5), which matches the literature values.[222, 233]

*Preparation of N^1,N^4-bis(2-pyridinylmethyl)-1,4-diaminobenzene (**4.21**)*

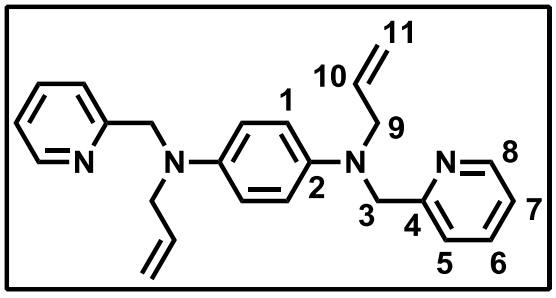
$NaBH_4$ (0.50 g, 13 mmol) was added portionwise to a solution of **4.20** (1.15 g, 4 mmol) in dry methanol (50 ml) at 0^oC and then the mixture was stirred at room temperature for 24 hours. The methanol was then evaporated *in vacuo*. 100 ml of water was added to the concentrated solution followed by 3x50 ml dichloromethane extraction. The organic layer was collected and dried over $MgSO_4$. Evaporating the dichloromethane *in vacuo* gave pure **4.21** as a light yellow powder (1.09 g, 94%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.39 (4H, s, H3), 6.60 (4H, s, H1), 7.16 (2H, dd, J = 7.5, 4.2 Hz, H6), 7.34 (2H, d, J = 8.1 Hz, H8), 7.63 (2H, dd, J = 7.8, 7.5 Hz, H7), 8.57 (2H, d, J = 4.8 Hz, H5).



4.21

*Preparation of N^1,N^4-diallyl-N^1,N^4-bis(2-pyridinylmethyl)-1,4-diaminobenzene (**4.14**)*

A mixture of **4.21** (1.45 g, 5 mmol) and NaH (0.24 g, 10 mmol) was stirred in dry THF (50 ml) at 0^oC. Allylbromide (0.87 ml, 10 mmol) was added dropwise to the mixture. The mixture was warmed to room temperature and refluxed for two days. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1M aqueous NH_4Cl solution. The organic layer was extracted with 3x40 ml of diethyl ether. The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation of diethyl ether under reduced pressure gave an impure brown oily liquid. Purification of the crude product with silica gel column chromatography using 30:70 (ethyl acetate:petroleum ether) solvent ratio gave **4.14** as a yellow brown oily liquid that crystallized on standing (0.69



4.14

g, 63%), m.p. 78-79^{o}C. ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 3.95 (4H, d, J = 2.5 Hz, H9), 4.53 (4H, s, H3), 5.15 (2H, d, J = 10.0 Hz, H11), 5.20 (2H, d, J = 17.5 Hz, H11'), 5.83-5.90 (2H, m, H10), 6.62 (4H, s, H1), 7.13 (2H, dd, J = 7.0, 5.5 Hz, H7), 7.28 (2H, d, J = 7.5 Hz, H5), 7.58 (2H, t, J = 7.5 Hz, H6), 8.55 (2H, d, J = 5.0 Hz, H8). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 54.78 C9, 57.11 C3, 114.80 C1, 116.86 C11, 121.35 C5, 121.85 C7, 134.09 C10, 136.86 C6, 140.87 C2, 149.10 C8, 159.77 C4. Elem. Anal. found: C, 77.67; H, 7.13; N15.40. Calc. for $C_{24}H_{26}N_4$: C 77.80; H 7.07; N 15.12. ESI-MS: found M = 370.2146; $C_{24}H_{26}N_4$ requires M = 370.2152. IR (cm^{-1}) 3078, 3048, 3006, 2910, 1837, 1679, 1640, 1590, 1568, 1518, 1469, 1434, 1415, 1380, 1356, 1227, 1186, 1145, 1091, 1072,1045, 992, 958, 941, 926, 812, 759, 728, 657.

6.2 Complex preparation

Complex of 8-allyloxyquinoline

With silver(I) perchlorate (3sw74) **2.15**

8-Allyloxyquinoline (0.0947 g, 0.5 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) perchlorate (0.2120 g, 1 mmol) in acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of golden crystals suitable for single crystal X-ray analysis. Yield 0.0525 g, 27%. m.p. 138-140^{o}C. Elem. Anal. found: C, 37.12; H, 2.81; N, 3.51. Calc. for $C_{12}H_{11}NOAgClO_4$: C, 36.72; H, 2.82; N, 3.57 revealing a 1:1 (ligand:silver) ratio complex.

Complex of 6-allyloxyquinoline

With silver(I) triflate (3sw75) **2.16**

6-Allyloxyquinoline (0.0926 g, 0.5 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.2570 g, 1 mmol) in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.1912 g, 86%. m.p. 133-135^{o}C. Elem. Anal. found: C, 35.19; H, 2.39; N, 3.22. Calc. for

$C_{12}H_{11}NOAgSO_3CF_3$: C, 35.31; H, 2.51; N, 3.17 revealing a 1:1 (ligand:silver) ratio complex.

Complexes of p-allyloxyazobenzene

With silver(I) perchlorate (3sw74-2) **2.17**

p-Allyloxyazobenzene (0.0953 g, 0.4 mmol) was dissolved in 1 ml toluene and was added to a solution of silver(I) perchlorate (0.1659 g, 0.8 mmol) in 1 ml acetone. The mixture was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the mixture. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0820 g, 46%. m.p. 109-111^{o}C. Elem. Anal. found: C, 40.76; H, 3.30; N, 6.58. Calc. for $C_{15}H_{14}N_2OAgClO_4$: C, 40.43; H, 3.17; N, 6.29 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) nitrate (3sw63) **2.18**

p-Allyloxyazobenzene (0.0952 g, 0.4 mmol) was dissolved in 1 ml acetone and was added to silver(I) nitrate (0.1360 g, 0.8 mmol) dissolved in 0.5 ml water. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. Red crystals suitable for single crystal X-ray analysis were obtained after two weeks. Yield 0.0290 g, 18%. m.p. 84-86^{o}C. Elem. Anal. found: C, 44.36; H, 3.43; N, 10.40. Calc. for $C_{15}H_{14}N_2OAgNO_3$: C, 44.14; H, 3.46; N, 10.30 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) tetrafluoroborate (3sw67) **2.19**

p-Allyloxyazobenzene (0.0953 g, 0.4 mmol) was dissolved in 1 ml acetone and was added to silver(I) tetrafluoroborate (0.1557 g, 0.8 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of red crystals suitable for single crystal X-ray analysis. Yield 0.0501 g, 29%. m.p. 139-141^{o}C. Elem. Anal. found: C, 41.57; H, 3.35; N, 6.29. Calc. for $C_{15}H_{14}N_2OAgBF_4$: C, 41.61; H, 3.26; N, 6.47 revealing a 1:1 (ligand:silver) ratio complex.

Complex of 4,4'-di(allyloxy)benzophenone

With silver(I) perchlorate (3sw78) **2.33**

4,4'-Di(allyloxy)benzophenone (0.0589 g, 0.2 mmol) was dissolved in 2 ml of (1:2 benzene:toluene) mixture and was added to silver(I) perchlorate (0.0829 g, 0.4 mmol) dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis after a week. Yield 0.0903 g, 90%. m.p. 98-100^{o}C. Elem. Anal. found: C, 45.70; H, 3.54. Calc. for $C_{19}H_{18}O_3AgClO_4$: C, 45.49; H, 3.62 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) hexafluorosilicate (3sw83) **2.34**

4,4'-Di(allyloxy)benzophenone (0.0589 g, 0.2 mmol) was dissolved in xylene/acetone mixture and was added to silver(I) tetrafluoroborate (0.0779 g, 0.4 mmol) solution in acetone. The solution was kept in darkness at room temperature, where the xylene/acetone solvent was allowed to evaporate slowly over two weeks. During this time the tetrafluoroborate anion decomposed to form HF that resulted in the growth of small crystals of **2.34**. m.p. 169-171^{o}C. Elem. Anal. found: C, 34.69; H, 3.29. Calc. for $C_{19}H_{18}O_3.Ag_2SiF_6.2H_2O.\frac{1}{2}CH_3COCH_3$: C, 34.33; H, 3.51 revealing 1:1 (ligand:silver) ratio complex.

Complex of 9,9'-bis(4-allyloxyphenyl)fluorene

With silver(I) perchlorate (3sw88) **2.35**

9,9'-Bis(4-allyloxyphenyl)fluorene (0.0215 g, 0.05 mmol) was dissolved in 1 ml of nitromethane and was added to a solution of silver(I) perchlorate (0.0207 g, 0.1 mmol) in 1 ml nitromethane. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis after three days. Yield 0.0145 g, 45%. m.p. 111-113^{o}C. Elem. Anal.

found: C, 58.15; H, 4.28. Calc. for $C_{31}H_{26}O_2AgClO_4$: C, 58.37; H, 4.11 revealing a 1:1(ligand:silver) ratio complex.

Complex of the diallylether of bisphenol A

With silver (I) tetrafluoroborate (3sw66) **2.36**

The diallylether of bisphenol A (0.1209 g, 0.4 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) tetrafluoroborate (0.1557 g, 0.8 mmol) in 1 ml acetone. Diethyl ether diffusion into the reaction mixture enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0415 g, 21%. m.p. 149-151^{o}C. Elem. Anal. found: C, 48.47; H, 4.83. Calc. for $C_{21}H_{25}O_2AgBF_4.H_2O$: C, 48.40; H, 5.03 revealing a 1:1 (ligand:silver) ratio complex.

Complex of cyclohexylidenedi(4-allyloxyphenyl)methane

With silver(I)perchlorate (3sw104) **2.37**

Cyclohexylidenedi(4-allyloxyphenyl)methane (0.1442 g, 0.4 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) perchlorate (0.1659 g, 0.8 mmol) in 1 ml acetone. Diethyl ether diffusion into the reaction mixture, while in darkness at room temperature, resulted in the growth of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.1258 g, 55%. m.p. 123-125^{o}C. Elem. Anal. found: C, 52.12; H, 5.04. Calc. for $C_{25}H_{28}O_2AgClO_4.\frac{1}{2}H_2O$: C, 52.06; H, 5.07 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) triflate (3sw91) **2.38**

Cyclohexylidenedi(4-allyloxyphenyl)methane (0.0721 g, 0.2 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.1028 g, 0.4 mmol) solution in 1 ml acetone. Diethyl ether diffusion into the reaction mixture, while in darkness at room temperature afforded the growth of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0123 g, 19%. m.p. 45-47^{o}C. Elem. Anal. found: C, 49.48; H, 4.96. Calc. for

$C_{25}H_{28}AgSO_3CF_3.H_2O$: C, 49.14; H, 4.76 revealing a 1:1 (ligand:silver) ratio complex that contains one water molecule.

Complex of the diallylether of bisphenol P

With silver(I) tetrafluoroborate (3sw39-1) **2.39**

The diallylether of bisphenol P (0.1706 g, 0.4 mmol) was dissolved in 1 ml acetone and was added to silver(I) tetrafluoroborate (0.0779 g, 0.4 mmol) solution in acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.1278 g, 51%. m.p. 119-121^{o}C. Elem. Anal. found: C, 57.64; H, 5.38. Calc. for $C_{30}H_{34}O_2AgBF_4$: C, 58.00; H, 5.52 revealing a 1:1 (ligand:silver) ratio complex.

Complex of *2*,4,6-tris(4-allyloxyphenoxy)-1,3,5-triazine

With silver(I) perchlorate (3sw49) **2.50**

2,4,6-Tris(4-allyloxyphenoxy)-1,3,5-triazine (0.0071 g, 0.0135 mmol) was dissolved in 1 ml of acetone and was added to a solution of silver(I) perchlorate (0.0056 g, 0.0027 mmol) in 1 ml acetone. Diethyl ether diffusion into the reaction mixture, while in darkness at room temperature, afforded colourless crystals suitable for single crystal X-ray structure analysis after two weeks. Yield 0.0031 g, 24%. m.p. explodes at 114^{o}C-116^{o}C. Not enough sample for further characterisation.

Complex of 1,3,5-tris(allyloxymethyl)-2,4,6-trimethylbenzene

With silver(I) triflate (3sw86) **2.49**

1,3,5-Tris(allyloxymethyl)-2,4,6-trimethylbenzene (0.0331 g, 0.1 mmol) was dissolved in 1 ml of acetone and was added to silver(I) triflate (0.1028 g, 0.4 mmol) dissolved in 1 ml toluene. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis after two weeks. Yield 0.0416 g, 29%. m.p. 135-137^{o}C. Elem. Anal.

found: C, 39.58; H, 4.31. Calc. for $C_{42}H_{60}O_6.3Ag(SO_3CF_3).2CH_3COCH_3$: C, 39.57; H, 4.69 revealing a 2:3 (ligand:silver) ratio complex with 2 molecules of acetone.

Complex of 2,2',4,4'-tetraallyloxybenzophenone

With silver(I) perchlorate (3sw80) **2.69**

2,2',4,4'-Tetraallyloxybenzophenone (0.0122 g, 0.03 mmol) was dissolved in 1 ml toluene and was added to a solution of silver(I) perchlorate (0.0249 g, 0.12 mmol) in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0152 g, 60%. m.p. 79-81^{o}C. Elem. Anal. found: C, 35.58; H, 3.70. Calc. for $C_{25}H_{26}O_5.2AgClO_4.H_2O$: C, 35.78; H, 3.36 revealing a 1:2 (ligand:silver) ratio complex.

With silver(I) triflate (3sw84) **2.70**

2,2',4,4'-Tetraallyloxybenzophenone (0.0121 g, 0.03 mmol) was dissolved in 1 ml xylene and was added to silver(I) triflate (0.0308 g, 0.12 mmol) dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0105 g, 38%. m.p. 62-64^{o}C. Elem. Anal. found: C, 33.86; H, 2.75. Calc. for $C_{25}H_{26}O_5.2AgSO_3CF_3.2H_2O$: C, 33.91; H, 3.16 revealing a 1:2 (ligand:silver) ratio complex.

Complex of bis(2,4-diallyloxyphenyl)methane

With silver(I) perchlorate (3sw100) **2.71**

Bis(2,4-diallyloxyphenyl)methane (0.0196 g, 0.05 mmol) was dissolved in 1 ml nitromethane and was added to silver(I) perchlorate (0.0415 g, 0.2 mmol) dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray

structure analysis. Yield 0.0299 g, 74%. m.p. 149-151^{o}C. Elem. Anal. found: C, 36.18; H, 3.82. Calc. for $C_{25}H_{28}O_4.2AgClO_4.H_2O$: C, 36.39; H, 3.66 revealing a 1:2 (ligand:silver) ratio complex.

Complexes of 1,1,2,2-tetrakis(4-allyloxyphenyl)ethene

With silver(I) perchlorate (3sw90) **2.72**

1,1,2,2-Tetrakis(4-allyloxyphenyl)ethene (0.0321 g, 0.06 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.0598 g, 0.29 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. The X-ray structure showed a rearranged product. Yield 0.0156 g, 26%. m.p. 95-97^{o}C. Elem. Anal. found: C, 42.46; H, 3.30. Calc. for $C_{35}H_{30}O_4.2AgClO_4.3H_2O$: C, 42.75; H, 3.69 revealing a 1:2 (rearranged ligand:silver) ratio complex. Powder diffraction fitted well with the calculated one. ^{1}H N.M.R. (500MHz, CD_3CN): δ 4.51 (4H, d, J = 5.0 Hz), 4.79 (2H, d, J = 5.5 Hz), 5.25-5.52 (6H, m), 6.02-6.10 (2H, m), 6.13-6.20 (1H, m), 6.78-6.82 (3H, m), 7.02-7.08 (3H, m), 7.17 (1H, d, J = 9.5 Hz), 7.31 (1H, d, J = 9.0 Hz), 8.11 (1H, s), 8.65 (1H, d, J = 9.5 Hz). ESI-MS: found MAg^+ = 621.1201; $C_{35}H_{30}O_4Ag$ requires MAg^+ = 621.1190.

With silver(I) perchlorate in acetonitrile (3sw93) **2.72a**

During an attempt to study the reaction of 1,1,2,2-tetrakis(4-allyloxyphenyl)ethene with silver(I) perchlorate in deuterated acetonitile solution, small crystals were grown. Further characterization was not carried out due to insufficient sample.

With silver(I) triflate (3sw92) **2.73**

1,1,2,2-Tetrakis(4-allyloxyphenyl)ethene (0.0556 g, 0.1 mmol) was dissolved in 1 ml nitromethane and was added to a solution of silver(I) triflate (0.1285 g, 0.5 mmol) in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of plate crystals, which were not suitable for single

crystal X-ray analysis. The data was poor, consequently the refinement was very poor (R_1=18%). m.p. 110-112^{o}C. Due to the poor refinement of the X-ray crystal structure, no further characterisation took place.

Complexes of 1,1,2,2-tetrakis(4-allyloxyphenyl)ethene

With silver(I) tetrafluoroborate (3sw98) **2.74**

1,1,2,2-Tetrakis(4-allyloxyphenyl)ethene (0.0374 g, 0.067 mmol) was dissolved in 1 ml acetone and was added to silver(I) tetrafluoroborate (0.0524 g, 0.269 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0454 g, 71%. m.p. 109-111^{o}C. Elem. Anal. found: C, 37.14; H, 3.68. Calc. for $C_{38}H_{36}O_4.3AgBF_4.5H_2O$: C, 37.08; H, 3.77 revealing a 1:3 (ligand:silver) ratio complex, which is different from the 1:2 (ligand:silver) ratio observed in the X-ray crystal structure.

Complex of 1,4-bis(bis(4-allyloxyphenyl)methylidene)cyclohexane

With silver(I) triflate (3sw94) **2.75**

1,4-Bis(bis(4-allyloxyphenyl)methylidene)cyclohexane (0.0252 g, 0.04 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.0407 g, 0.16 mmol) solution in acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0231 g, 51%. m.p. 77-79^{o}C. Elem. Anal. found: C, 45.80; H, 4.18. Calc. for $C_{44}H_{44}O_4.2AgSO_3CF_3.3H_2O$: C, 45.86; H, 4.18 revealing a 1:2 (ligand:silver) ratio complex.

Complex of hexakis(allyloxymethyl)benzene

With silver(I) perchlorate (3sw99) **2.76**

Hexakis(allyloxymethyl)benzene (0.0249 g, 0.05 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) perchlorate (0.0311 g, 0.15 mmol) in 1 ml acetone. The solution was left in darkness at room

temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0197 g, 43%. m.p. 89-91^{o}C. Elem. Anal. found: C, 38.30; H, 4.46. Calc. for $C_{30}H_{44}O_6.2AgClO_4.H_2O$: C, 38.69; H, 4.76 revealing a 1:2 (ligand:silver) ratio complex.

Complex of N,N-diallylaminobenzene

With silver(I) perchlorate (3sw40,3t) **3.18**

N,N-Diallylaminobenzene (0.0173 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.0415 g, 0.2 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0205 g, 54%. m.p. 123-125^{o}C. Elem. Anal. found: C, 37.99; H, 4.03; N, 3.95. Calc. $C_{12}H_{15}N.AgClO_4$: for C, 37.87; H, 3.97; N, 3.68 revealing a 1:1 (ligand:silver) ratio complex.

Complex of 2-(N,N-diallylamino)pyridine

With silver(I) perchlorate (3sw45 -3y) **3.19**

2-(N,N-Diallylamino)pyridine (0.0348 g, 0.2 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.0829 g, 0.4 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0562 g, 74%. m.p. 89-91^{o}C. Elem. Anal. found: C, 34.93; H, 3.77; N, 6.78. Calc. for $C_{11}H_{14}N_{2.}AgClO_4$: C, 34.63; H, 3.70; N, 7.34 revealing a 1:1 (ligand:silver) ratio complex.

Complexes of 2-(N,N-diallylamino)pyrimidine

With silver(I) perchlorate (3sw43/3s) **3.20**

2-(N,N-Diallylamino)pyrimidine (0.0175 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.0415 g, 0.2 mmol) in 1 ml

acetone, which formed a white precipitate instantaneously. The precipitate was dissolved in a mixture of THF, water and acetone. Slow evaporation of the solvent enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0166 g, 42%. m.p. 219-221^{o}C. Elem. Anal. found: C, 30.67; H, 3.24; N, 10.49. Calc. for $C_{10}H_{13}N_3AgClO_4.\frac{1}{2}H_2O$: C, 30.67; H, 3.60, N, 10.73 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) triflate (3sw42/3sw) **3.21**

2-(N,N-Diallylamino)pyrimidine (0.0177 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.0514 g, 0.2 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0358 g, 83%. m.p. 151-153^{o}C. Elem. Anal. found: C, 30.60; H, 2.96; N, 9.51. Calc. for $C_{10}H_{13}N_3AgSO_3CF_3$: C, 30.57; H, 3.03; N, 9.72 revealing a 1:1 (ligand:silver) ratio complex.

Complex of 2-(N,N-diallylamino)thiazole

With silver (I) triflate (3sw55) **3.22**

2-(N,N-Diallylamino)thiazole (0.0180 g, 0.1 mmol) was dissolved in 1 ml toluene and was added to a solution of silver(I) triflate (0.0514 g, 0.2 mmol) in toluene. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0156 g, 36%. m.p. 109-111^{o}C. Elem. Anal. found: C, 27.40; H, 2.68; N, 6.31. Calc. for $C_9H_{12}N_2S.AgSO_3CF_3$: C, 27.47; H, 2.77; N, 6.41 revealing a 1:1 (ligand:silver) ratio complex.

Complex of 8-diallylaminoquinoline

With silver (I) perchlorate (3sw56) **3.23**

8-Diallylaminoquinoline (0.0226 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.0415 g, 0.2 mmol) also dissolved in

1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0257 g, 59%. m.p. 149-151^{o}C. Elem. Anal. found: C, 41.45; H, 3.78; N, 6.21. Calc. for $C_{15}H_{16}N_2AgClO_4$: C, 41.74; H, 3.74; N, 6.49 revealing a 1:1 (ligand:silver) ratio complex.

Protonated salt of N^1,N^1,N^4,N^4-tetraallyl-1,4-diaminobenzene

From silver(I) perchlorate (3sw70) **3.25a**

N^1,N^1,N^4,N^4-Tetraallyl-1,4-diaminobenzene (0.0268 g, 0.1 mmol) was added to a solution of silver(I) perchlorate (0.0829 g, 0.4 mmol) in acetone. Two drops of perchloric acid was added to the mixture and left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. Needle shaped crystals were obtained and single crystal X-ray structure analysis carried out.

Protonated salt of N^1,N^1,N^5,N^5-tetraallyl-1,5-diaminonaphthalene

From silver(I) perchlorate (3sw38) **3.31a**

N^1,N^1,N^5,N^5-Tetraallyl-1,5-diaminonaphthalene (0.03185 g, 0.10mmol) was added to a solution of silver(I) perchlorate (0.0415 g, 0.2 mmol) in acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of dark crystals suitable for single crystal X-ray structure analysis.

Complex of 2,4-bis(diallylamino)-6-chloro-1,3,5-triazine

With silver (I) perchlorate (3sw48) **3.32**

2,4-Bis(diallylamino)-6-chloro-1,3,5-triazine (0.0306 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) perchlorate (0.0415 g, 0.2 mmol) in acetone, which formed a white precipitate instantaneously. The precipitate was dissolved in a mixture of THF, water and acetone. Slow evaporation of the solvent over a period of time resulted in the isolation of colourless crystals suitable for single crystal X-ray structure

analysis. Yield 0.0105 g, 15%. m.p. 259-261^{o}C (explode). Elem. Anal. found: C, 25.89; H, 2.83; N, 9.22. Calc. for $C_{15}H_{20}N_5Cl.2AgClO_4.\frac{1}{2}CH_3COCH_3.\frac{1}{2}H_2O$: C, 26.13; H, 3.19; N, 9.23 revealing 1:2 (ligand:silver) ratio complex.

With silver(I) triflate (3sw 102) **3.33**

2,4-Bis(diallylamino)-6-chloro-1,3,5-triazine (0.0306 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.0514 g, 0.2 mmol) also dissolved in 1 ml acetone, which formed a white precipitate instantaneously. The precipitate was dissolved in a mixture of THF, water and acetone. Slow evaporation of the solvent resulted in the growth of crystals suitable for single crystal X-ray analysis. Yield 0.0642 g, 78%. m.p. 174-176^{o}C. Elem. Anal. found: C, 27.04; H, 2.69; N, 8.65. Calc. for $C_{15}H_{20}N_5OH.2AgSO_3CF_3.\frac{1}{2}CH_3COCH_3$: C, 26.76; H, 2.91; N, 8.43 revealing the chlorine atom of the ligand replaced by a hydroxyl group.

Complexes of 2,4,6-tris(diallylamino)pyrimidine

With silver(I) triflate (3sw37) **3.37**

2,4,6-Tris(diallylamino)pyrimidine (0.0366 g, 0.1 mmol) was dissolved in 1 ml dichloromethane and was added to a solution of silver(I) triflate (0.0771 g, 0.3 mmol) in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0495 g, 56%. m.p. 128-130^{o}C. Elem. Anal. found: C, 35.01, H, 3.95; N, 7.67. Calc. for $C_{22}H_{31}N_5.2AgSO_3CF_3.CH_3COCH_3$: C, 34.59; H, 3.98; N, 7.47 revealing a 1:2 (ligand:silver) ratio complex.

Complexes of 2,4,6-tris(diallylamino)-1,3,5-triazine

With silver(I) perchlorate (3sw53) **3.38**

2,4,6-Tris(diallylamino)-1,3,5-triazine (0.0635 g, 0.17 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.1075 g, 0.52 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This

enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0789 g, 59%. m.p. 119-121^{o}C. Elem. Anal. found: C, 32.46; H, 3.76; N, 10.88. Calc. for $C_{21}H_{30}N_6.2AgClO_4$: C, 32.29; H, 3.87; N, 10.76 revealing a 1:2 (ligand:silver) ratio complex.

With silver(I) triflate (3sw50) **3.39**

2,4,6-Tris(diallylamino)-1,3,5-triazine (0.0367 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.0771 g, 0.3 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0752 g, 66%. m.p. 159-161^{o}C. Elem. Anal. found: C, 25.75; H, 2.78; N, 7.61. Calc. for $C_{21}H_{30}N_6.3AgSO_3CF_3$: C, 25.35; H, 2.66; N, 7.39 revealing a 1:3 (ligand:silver) ratio complex.

Complexes of 1,3-diallylurea

With silver(I) triflate (3sw26) **4.22**

1,3-Diallylurea (0.0280 g, 0.2 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.1026 g, 0.4 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where petroleum ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0245 g, 31%. m.p. 119-121^{o}C. Elem. Anal. found: C, 24.40; H, 2.99; N, 6.95. Calc. for $C_7H_{12}N_{2.}AgSO_3CF_3$: C, 24.20; H, 3.05; N, 7.05 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) tetrafluoroborate (3sw17) **4.23**

1,3-Diallylurea (0.0140 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) tetrafluoroborate (0.0195 g, 0.1 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where petroleum ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0256 g, 76%. m.p. 137-139^{o}C . Elem. Anal. found: C, 24.98;

H, 3.99; N, 8.75. Calc. for $C_7H_{12}N_2O.AgBF_4$: C, 25.11; H, 3.61; N, 8.37 revealing a 1:1 (ligand:silver) ratio complex.

Complexes of 1,3-diallylbenzimidazol-2-one

With silver(I) perchlorate (3sw79) **4.24**

1,3-Diallylbenzimidazol-2-one (0.0215 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.0208 g, 0.1 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0378 g, 90%. m.p. 139-141^{o}C. Elem. Anal. found: C, 37.18; H, 3.22; N, 6.59. Calc. for $C_{13}H_{14}N_2O.AgClO_4$: C, 37.04; H, 3.35; N, 6.64 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) triflate (3sw82) **4.25**

1,3-Diallylbenzimidazol-2-one (0.0216 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) triflate (0.0258 g, 0.1 mmol) also dissolved in acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0319 g, 68%. m.p. 69-71^{o}C. Elem. Anal. found: C, 34.51; H, 3.12; N, 5.74. Calc. for $C_{13}H_{14}N_2O.AgSO_3CF_3.H_2O$: C, 34.37; H, 3.30; N, 5.73 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) tetrafluoroborate (3sw81) **4.26**

1,3-Diallylbenzimidazol-2-one (0.0218 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) tetrafluoroborate (0.0195 g, 0.1 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0127 g, 31%. m.p. 179-181^{o}C. Elem. Anal. found: C, 38.57; H, 3.32; N, 6.88. Calc. for $C_{13}H_{14}N_2O.AgBF_4$: C, 38.18; H, 3.45; N, 6.85 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) hexafluorophosphate (3sw85-1) **4.27**

1,3-Diallylbenzimidazol-2-one (0.0213 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) hexafluorophosphate (0.0253 g, 0.1 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0134 g, 29%. m.p. 109-111^{o}C. Elem. Anal. found: C, 33.50; H, 3.21; N, 6.10. Calc. for $C_{13}H_{14}N_2O.AgPF_6$: C, 33.43; H, 3.02; N, 6.00 revealing a 1:1 (ligand:silver) ratio complex.

Complex of diallyldimethylsilane

With silver(I) triflate (3sw23) **4.28**

Diallyldimethylsilane (0.073 ml, 0.4 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.1028 g, 0.4 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where petroleum ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0962 g, 61%. m.p. 79-81^{o}C. Elem. Anal. found: C, 27.48; H, 4.30. Calc. for $SiC_8H_{16.}AgSO_3CF_3$: C, 27.21; H, 4.06 revealing 1:1 (ligand:silver) ratio complex.

Complexes of 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione

With silver(I) hexafluorophosphate (3sw69-1) **4.29**

1,3,5-Triallyl-1,3,5-triazine-2,4,6-trione (0.086 ml, 0.4 mmol) was dissolved in 1 ml acetone and was added to silver(I) hexafluorophosphate (0.3034 g, 1.2 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.1056 g, 53%. m.p. 79-81^{o}C. Elem. Anal. found: C, 27.39; H, 3.35; N, 7.80. Calc. for $C_{12}H_{15}N_3O_{3.}AgPF_6.H_2O$: C, 27.71; H, 3.29; N, 8.08 revealing a 1:1 (ligand:silver) ratio complex.

With silver(I) nitrate (3sw65) **4.30**

1,3,5-Triallyl-1,3,5-triazine-2,4,6-trione (0.086 ml, 0.4 mmol) was added to silver(I) nitrate (0.2038 g, 1.2 mmol) solution dissolved in 1 ml water. Slow evaporation of the water over time enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0568 g, 34%. m.p. 114-116^{o}C. Elem. Anal. found: C, 34.42; H, 3.59; N, 13.35. Calc. for $C_{12}H_{15}N_3O_3.AgNO_3$: C, 34.39; H, 3.61; N, 13.37 revealing a 1:1 (ligand:silver) ratio complex.

Complexes of 1,1,3,3-tetraallylurea

With silver(I) perchlorate (3sw28) **4.31**

1,1,3,3-Tetraallylurea (0.0220 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) perchlorate (0.0415 g, 0.2 mmol) in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0495 g, 78%. m.p. 139-141^{o}C. Elem. Anal. found: C, 24.95; H, 3.13; N, 4.44. Calc. for $C_{13}H_{20}N_2O.2AgClO_4$: C, 24.59; H, 3.17; N, 4.41 revealing a 1:2 (ligand:silver) ratio complex.

With silver(I) triflate (3sw31) **4.32**

1,1,3,3-Tetraallylurea (0.0219 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.0514 g, 0.2 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0634 g, 51%. m.p. 59-61^{o}C. Elem. Anal. found: C, 16.56; H, 1.95; N, 2.36. Calc. for $C_{13}H_{20}N_2O.4Ag(SO_3CF_3)$: C, 16.36; H, 1.62; N, 2.24 revealing a 1:4 (ligand:silver) ratio complex.

With silver(I) tetrafluoroborate (3sw32) **4.33**

1,1,3,3-Tetraallylurea (0.0223 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to a solution of silver(I) tetrafluoroborate (0.0389 g, 0.2 mmol) in acetone. The solution was left in darkness at room temperature, where diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0361 g, 59%. m.p. 85-87^{o}C. Elem. Anal. found: C, 25.21; H, 3.76; N, 4.47. Calc. for $C_{13}H_{22}N_2O.2AgBF_4.H_2O$: C, 24.88; H, 3.53, N, 4.46 revealing a 1:2 (ligand:silver) ratio complex.

Appendix

Crystallography

Tables A – R list the crystal data and X-ray experimental details for the fifty four crystal structures discussed in this thesis. Throughout the text, selected bond lengths and angles are discussed and listed under the appropriate figures, while the remaining distances and angles, as well as atomic coordinates are available on request from the Department of Chemistry, University of Canterbury.

X-Ray crystallographic data collection and refinement was carried out with either a Bruker APEXII instrument, using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, or an Oxford-Agilent SuperNova instrument with focused microsource Cu Kα (λ = 1.5418 Å) radiation and ATLAS CCD area detector. All structures were solved using direct methods with SHELXS[234] and refined on *F*2 using all data by full matrix least-squares procedures with SHELXL.[235] Unless otherwise stated all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 or 1.5 times the isotropic equivalent of their carrier carbon atoms. Some of the refinements reported may change a little upon preparation for final publication.

X-Ray Powder Diffraction

X-Ray Powder Diffraction data were collected using an Oxford-Agilent SuperNova instrument using Cu Kα (λ = 1.5418 Å) radiation and an ATLAS CCD area detector. Samples were prepared by grinding *ca*. 5 mg of analyte with a minimum quantity of Paratone-N oil and applying a sample of approximately 0.5 mm diameter to a thin glass fibre mounted on a ginometer head, which was mounted directly in the beam path. Diffraction data was recorded using four averaged 360^{o} scans in Φ with 150 second exposure time per rotation frame. The diffraction data were integrated radially and a background correction manually applied, using a 6th order polynomial to approximate the absorbance due to the fibre and oil.

Table A. Crystal data and sructure refinement for **2.15, 2.16** and **2.17**

Compound	3sw74 **2.15**	3sw75 **2.16**	3sw74-2 **2.17**
Empirical formula	$C_{12}H_{11}NO_5ClAg$	$C_{13}H_{11}NO_4F_3SAg$	$C_{15}H_{14}N_2O_5ClAg$
Formula weight	392.54	442.16	445.60
Temperature	112.15	114.15	113.15
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1
Unit cell dimensions: a/Å	9.1546(4)	7.5472(3)	8.6313(3)
b/Å	17.5089(6)	13.0293(4)	8.7450(3)
c/Å	7.9704(3)	15.5377(5)	10.6605(4)
α/°	90.00	88.778(2)	84.336(2)
β/°	97.136(2)	89.792(2)	78.765(2)
γ/°	90.00	77.169(2)	84.258(2)
Volume/$Å^3$	1267.66(9)	1489.40(9)	782.69(5)
Z	4	4	2
Density (calculated) Mg/m^3	2.057	1.972	1.891
Absorption coefficient mm^{-1}	1.819	1.545	1.487
F(000)	776	872	444
Crystal size/mm^3	0.45 × 0.28 × 0.1	0.3 × 0.2 × 0.06	0.23 × 0.2 × 0.06
Theta range for data collection (°)	5.66 to 53.94°	5.24 to 50.1°	5.62 to 55°
Reflections collected	27114	28065	17713
Independent reflections [R(int)]	2757[0.0498]	5261[0.0467]	3589[0.0465]
Completeness	99.5	99.9	99.9
Data/restraints/parameters	2757/0/181	5261/0/415	3589/0/217
Goodness-of-fit on F^2	1.014	1.107	1.073
Final R_1 indices [I>2sigma (I)]	$R_1 = 0.0264$, $wR_2 = 0.0640$	$R_1 = 0.0352$, $wR_2 = 0.0891$	$R_1 = 0.0325$, $wR_2 = 0.0823$
Final R indices [all data]	$R_1 = 0.0342$, $wR_2 = 0.0661$	$R_1 = 0.0459$, $wR_2 = 0.0930$	$R_1 = 0.0395$, $wR_2 = 0.0852$
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.52	0.88/-0.74	1.06/-0.91

Table B. Crystal data and structure refinement for **2.18, 2.19** and **2.33**

Compound	3sw63 **2.18**	3sw67 **2.19**	3sw78 **2.33**
Empirical formula	$C_{15}H_{14}N_3O_4Ag$	$C_{15}H_{14}BN_2OF_4Ag$	$C_{19}H_{18}O_7ClAg$
Formula weight	408.16	432.96	501.65
Temperature	117.15	118.15	113.15
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$
Unit cell dimensions: a/Å	8.2169(2)	8.3301(8)	10.2050(4)
b/Å	9.3901(3)	9.0956(8)	8.4325(3)
c/Å	10.7823(3)	10.2729(9)	22.5202(9)
α/°	96.889(2)	81.362(5)	90.00
β/°	109.792(2)	87.857(5)	98.830(2)
γ/°	103.877(2)	84.392(5)	90.00
Volume/$Å^3$	741.29(4)	765.63(12)	1914.98(13)
Z	2	2	4
Density (calculated) Mg/m^3	1.829	1.878	1.740
Absorption coefficient mm^{-1}	1.384	1.365	1.231
F(000)	408	428	1008
Crystal size/mm^3	0.5 × 0.4 × 0.2	0.5 × 0.5 × 0.4	0.35 × 0.2 × 0.18
Theta range for data collection (°)	5.44 to 55°	4.92 to 54°	5.86 to 55°
Reflections collected	16775	14785	41244
Independent reflections [R(int)]	3402[0.0400]	3277[0.0560]	4399[0.0847]
Completeness	99.9	98.3	99.9
Data/restraints/parameters	3402/0/208	3277/0/227	4399/0/253
Goodness-of-fit on F^2	1.040	1.280	0.858
Final R_1 indices [I>2sigma (I)]	$R_1 = 0.0219$, $wR_2 = 0.0528$	$R_1 = 0.0664$, $wR_2 = 0.1581$	$R_1 = 0.0303$, $wR_2 = 0.0501$
Final R indices [all data]	$R_1 = 0.0251$, $wR_2 = 0.0539$	$R_1 = 0.0741$, $wR_2 = 0.1616$	$R_1 = 0.0540$, $wR_2 = 0.0533$
Largest diff. peak/hole / e $Å^{-3}$	0.42/-0.38	1.08/-1.61	0.50/-0.59

Table C. Crystal data and structure refinement for **2.34, 2.35** and **2.36**

Compound	3sw83 **2.34**	3sw88 **2.35**	3sw66 **2.36**
Empirical formula	$C_{19}Ag_2F_6O_6H_{24}Si$	$C_{31}H_{26}O_6ClAg$	$C_{21}H_{24}BO_2F_4Ag$
Formula weight	706.21	637.84	503.08
Temperature	296.15	113.15	116.15
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	Pbca
Unit cell dimensions: a/Å	15.5763(6)	8.8520(4)	15.3174(7)
b/Å	13.0202(4)	23.7737(11)	12.4331(7)
c/Å	11.4150(4)	12.4514(5)	21.5666(11)
α/°	90.00	90.00	90.00
β/°	98.560(2)	92.715(2)	90.00
γ/°	90.00	90.00	90.00
Volume/$Å^3$	2289.25(14)	2617.4(2)	4107.2(4)
Z	4	4	8
Density (calculated) Mg/m^3	2.049	1.637	1.627
Absorption coefficient mm^{-1}	1.846	0.920	1.031
F(000)	1392	1312	2032
Crystal size/mm^3	0.5 × 0.4 × 0.1	0.5 × 0.44 × 0.3	0.4 × 0.06 × 0.05
Theta range for data collection (°)	4.1 to 55°	4.74 to 50.1°	5.32 to 53.76°
Reflections collected	52145	48499	80892
Independent reflections [R(int)]	5260[0.0471]	4629[0.0443]	4377[0.1575]
Completeness	99.9	100	98.9
Data/restraints/parameters	5260/0/331	4629/6/457	4377/0/290
Goodness-of-fit on F^2	0.969	1.069	1.003
Final R_1 indices [I>2sigma (I)]	$R_1 = 0.0211$, $wR_2 = 0.0470$	$R_1 = 0.0295$, $wR_2 = 0.0771$	$R_1 = 0.0581$, $wR_2 = 0.1435$
Final R indices [all data]	$R_1 = 0.0296$, $wR_2 = 0.0489$	$R_1 = 0.0381$, $wR_2 = 0.0814$	$R_1 = 0.1017$, $wR_2 = 0.1599$
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.54	0.75/-0.57	1.41/-1.62

Table D. Crystal data and structure refinement for **2.37, 2.38** and **2.39**

Compound	3sw104 **2.37**	3sw91 **2.38**	3sw34 (3pjs) **2.39**
Empirical formula	$C_{25}H_{28}O_6ClAg$	$C_{26}H_{30}O_6AgSF_3$	$C_{30}H_{34}BO_2F_4Ag$
Formula weight	567.79	635.43	621.25
Temperature	293(2)	293(2)	112.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/m$
Unit cell dimensions: a/Å	8.45899(15)	16.7946(5)	6.6479(2)
b/Å	23.4086(4)	13.5973(4)	35.1034(11)
c/Å	12.4297(2)	12.0811(4)	12.0452(4)
α/°	90.00	90.00	90.00
β/°	103.7403(18)	109.375(4)	92.018(2)
γ/°	90.00	90.00	90.00
Volume/$Å^3$	2390.82(7)	2602.61(14)	2809.17(15)
Z	4	4	4
Density (calculated) Mg/m^3	1.577	1.622	1.469
Absorption coefficient mm^{-1}	0.993	0.916	0.769
F(000)	1160	1296	1272
Crystal size/mm^3	0.36 × 0.23 × 0.14	0.25 × 0.15 × 0.11	0.5 × 0.46 × 0.32
Theta range for data collection (°)	5.26 to 50.1°	5.88 to 55°	4.64 to 50.1°
Reflections collected	22846	33410	54406
Independent reflections [R(int)]	4217[0.0306]	5973[0.0231]	5051[0.0409]
Completeness	100	100	99.9
Data/restraints/parameters	4217/0/339	5973/0/360	5051/0/401
Goodness-of-fit on F^2	1.059	1.058	1.471
Final R_1 indices [I>2sigma (I)]	$R_1 = 0.0325$, $wR_2 = 0.0824$	$R_1 = 0.0241$, $wR_2 = 0.0599$	$R_1 = 0.1012$, $wR_2 = 0.3154$
Final R indices [all data]	$R_1 = 0.0370$, $wR_2 = 0.0855$	$R_1 = 0.0289$, $wR_2 = 0.0634$	$R_1 = 0.1215$, $wR_2 = 0.3430$
Largest diff. peak/hole / e $Å^{-3}$	2.31/-0.62	0.62/-0.50	2.52/-1.31

Table E. Crystal data and structure refinement for **2.46, 2.48** and **2.49**

Compound	3sw96 **2.46**	3sw49 **2.50**	3sw86 **2.49**
Empirical formula	$C_{39}H_{42}O_6$	$C_{84}H_{78}Ag_4Cl_4N_6O_{36}$	$C_{45}H_{60}O_{15}F_9S_3Ag_3$
Formula weight	606.73	2320.80	1431.72
Temperature	293(2)	433.15	113.15
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/n$	C2/c
Unit cell dimensions: a/Å	9.9520(6)	10.9610(7)	20.0475(6)
b/Å	12.3627(8)	29.2788(19)	12.2300(4)
c/Å	14.7252(10)	14.9205(10)	22.5008(7)
α/°	76.007(6)	90.00	90.00
β/°	70.995(6)	96.749(4)	99.723(2)
γ/°	80.757(5)	90.00	90.00
Volume/$Å^3$	1655.49(18)	4755.2(5)	5437.5(3)
Z	2	2	4
Density (calculated) Mg/m^3	1.217	1.621	1.749
Absorption coefficient mm^{-1}	0.647	1.012	1.279
F(000)	648	2336	2880
Crystal size/mm^3	0.24 × 0.10 × 0.06	0.5 × 0.25 × 0.22	0.24 × 0.15 × 0.14
Theta range for data collection (°)	6.48 to 60°	3.08 to 53.6°	3.92 to 50.1°
Reflections collected	1654	57940	52390
Independent reflections [R(int)]	949[0.0184]	10112[0.1243]	4808[0.0982]
Completeness	99.9	99.6	100
Data/restraints/parameters	949/0/406	10112/0/607	4808/0/378
Goodness-of-fit on F^2	1.376	1.484	1.055
Final R_1 indices [I>2sigma (I)]	$R_1 = 0.0428$, $wR_2 = 0.1229$	$R_1 = 0.0978$, $wR_2 = 0.2367$	$R_1 = 0.0465$, $wR_2 = 0.1111$
Final R indices [all data]	$R_1 = 0.0466$, $wR_2 = 0.1272$	$R_1 = 0.1476$, $wR_2 = 0.2536$	$R_1 = 0.0563$, $wR_2 = 0.1180$
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.15	1.47/-1.49	0.75/-0.83

Table F. Crystal data and structure refinement for **2.54, 2.62** and **2.65**

Compound	3sw76 **2.54**	3sw87 **2.62**	3sw103 **2.65**
Empirical formula	$C_{25}H_{26}O_5$	$C_{38}H_{36}O_4$	$C_{44}H_{44}O_4$
Formula weight	406.46	556.67	636.79
Temperature	114.15	115.15	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions: a/Å	17.5970(8)	9.2476(3)	13.7594(5)
b/Å	7.3927(3)	24.8457(9)	5.23695(19)
c/Å	16.9737(8)	13.2688(5)	25.7442(12)
α/°	90.00	90.00	90.00
β/°	99.944(3)	99.980(2)	103.097(4)
γ/°	90.00	90.00	90.00
Volume/$Å^3$	2174.93(17)	3002.55(18)	1806.81(12)
Z	4	4	2
Density (calculated) Mg/m^3	1.241	1.231	1.170
Absorption coefficient mm^{-1}	0.086	0.079	0.073
F(000)	864	1184	680
Crystal size/mm^3	0.5 × 0.42 × 0.28	0.32 × 0.26 × 0.24	0.28 × 0.13 × 0.06
Theta range for data collection (°)	5.76 to 53.6°	3.52 to 53.64°	6.08 to 50.1°
Reflections collected	44845	63902	7241
Independent reflections [R(int)]	4645[0.0623]	6433[0.0956]	3196[0.0531]
Completeness	99.5	99.7	100
Data/restraints/parameters	4645/0/290	6433/0/380	3196/0/225
Goodness-of-fit on F^2	0.963	1.100	1.070
Final R_1 indices [I>2sigma (I)]	$R_1 = 0.0428$, $wR_2 = 0.1046$	$R_1 = 0.0621$, $wR_2 = 0.1332$	$R_1 = 0.0514$, $wR_2 = 0.1099$
Final R indices [all data]	$R_1 = 0.0688$, $wR_2 = 0.1144$	$R_1 = 0.0805$, $wR_2 = 0.1430$	$R_1 = 0.0850$, $wR_2 = 0.1325$
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.25	0.24/-0.24	0.24/-0.28

Table G. Crystal data and structure refinement for **2.69, 2.70** and **2.71**

Compound	3sw80 **2.69**	3sw84 **2.70**	3sw100 **2.71**
Empirical formula	$C_{25}H_{28}O_{14}Cl_2Ag_2$	$C_{27}H_{28}Ag_2F_6O_{11}S_2$	$C_{25}H_{28}O_{12}Cl_2Ag_2$
Formula weight	839.11	922.35	807.11
Temperature	296.15	296.15	293(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1
Unit cell dimensions: a/Å	14.9630(5)	9.0292(3)	8.2019(3)
b/Å	8.5572(3)	13.6504(4)	12.9678(3)
c/Å	22.0642(7)	14.2466(4)	12.9910(3)
α/°	90.00	65.688(2)	93.884(2)
β/°	92.507(2)	75.778(2)	97.313(2)
γ/°	90.00	77.050(2)	93.111(2)
Volume/$Å^3$	2822.43(16)	1536.06(8)	1364.59(6)
Z	4	2	2
Density (calculated) Mg/m^3	1.975	1.994	1.964
Absorption coefficient mm^{-1}	1.649	1.508	1.696
F(000)	1672	916	804
Crystal size/mm^3	0.49 × 0.1 × 0.08	0.32 × 0.16 × 0.12	0.20 × 0.04 × 0.01
Theta range for data collection (°)	5.46 to 55°	5.08 to 50.1°	5.58 to 54.98°
Reflections collected	62447	30190	48047
Independent reflections [R(int)]	6483[0.0651]	5436[0.0582]	6263[0.0245]
Completeness	100	100	100
Data/restraints/parameters	6483/2/396	5436/0/433	6263/0/430
Goodness-of-fit on F^2	1.192	0.928	1.053
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0465, wR_2 = 0.0778	R_1 = 0.0253, wR_2 = 0.0574	R_1 = 0.0195, wR_2 = 0.0466
Final R indices [all data]	R_1 = 0.0530, wR_2 = 0.0801	R_1 = 0.0316, wR_2 = 0.0598	R_1 = 0.0219, wR_2 = 0.0478
Largest diff. peak/hole / e $Å^{-3}$	0.69/-0.63	0.45/-0.63	0.68/-0.41

Table H. Crystal data and structure refinement for **2.72, 2.72a** and **2.73**

Compound	3sw90 **2.72**	3sw93 **2.72A**	3sw92 **2.73**
Empirical formula	$C_{266}H_{252}O_{56}Cl_7Ag_7$	$C_{42}H_{42}N_2O_8ClAg$	$C_{78}H_{72}O_{14}F_6S_2Ag_2$
Formula weight	5347.92	423.05	1627.22
Temperature	293(2)	120.01(10)	120.00(10)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	C2/c	P2/c
Unit cell dimensions: a/Å	9.4021(8)	17.3468(10)	24.4995(6)
b/Å	12.8069(11)	26.3851(6)	13.7300(3)
c/Å	15.4838(8)	10.5230(5)	21.1931(5)
α/°	100.628(6)	90.00	90.00
β/°	106.642(6)	124.412(8)	99.443(2)
γ/°	104.606(7)	90.00	90.00
Volume/$Å^3$	1661.0(2)	3973.5(3)	7032.3(3)
Z	1	4	4
Density (calculated) Mg/m^3	5.346	1.414	1.537
Absorption coefficient mm^{-1}	21.203	0.629	0.699
F(000)	2744	1744	3328
Crystal size/mm^3	0.20 × 0.05 × 0.04	0.21 × 0.04 × 0.03	0.21 × 0.06 × 0.03
Theta range for data collection (°)	6.2 to 147.72°	5.44 to 55°	5.38 to 52°
Reflections collected	11480	16040	43295
Independent reflections [R(int)]	6509[0.0551]	4529[0.0536]	13798[0.0410]
Completeness	97	99.0	100
Data/restraints/parameters	6509/0/461	4529/0/275	13798/0/968
Goodness-of-fit on F^2	1.319	1.023	2.541
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0733, wR_2 = 0.2065	R_1 = 0.0441, wR_2 = 0.0805	R_1 = 0.1299, wR_2 = 0.3571
Final R indices [all data]	R_1 = 0.0961, wR_2 = 0.2227	R_1 = 0.0644, wR_2 = 0.0871	R_1 = 0.1646, wR_2 = 0.3776
Largest diff. peak/hole / e $Å^{-3}$	1.38/-1.16	0.44/-0.53	3.42/-2.61

Table I. Crystal data and structure refinement for **2.74, 2.75** and **2.76**

Compound	3sw98 **2.74**	3sw94 **2.75**	3sw99 **2.76**
Empirical formula	$C_{76}H_{90}B_4O_{16}F_{16}Ag_4$	$C_{23}H_{24}O_6F_3SAg$	$C_{30}H_{42}O_{14}Cl_2Ag_2$
Formula weight	2038.20	593.35	913.28
Temperature	293(2)	120.01(10)	120(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	C2/c	$P2_1/n$
Unit cell dimensions: a/Å	9.5807(2)	31.1641(5)	8.52019(7)
b/Å	12.4096(2)	13.36139(12)	14.14393(14)
c/Å	34.8377(6)	12.12922(18)	13.85040(11)
α/°	90.00	90.00	90.00
β/°	95.9315(19)	110.9662(17)	90.8165(7)
γ/°	90.00	90.00	90.00
Volume/$Å^3$	4119.77(14)	4716.17(11)	1668.93(2)
Z	2	8	2
Density (calculated) Mg/m^3	1.643	1.671	1.817
Absorption coefficient mm^{-1}	1.036	1.004	1.402
F(000)	2052	2400	924
Crystal size/mm^3	0.40 × 0.32 × 0.10	0.17 × 0.15 × 0.09	0.4 × 0.04 × 0.02
Theta range for data collection (°)	5.38 to 55°	5.18 to 50.1°	5.58 to 50.1°
Reflections collected	66428	76277	36306
Independent reflections [R(int)]	18948[0.0278]	4174[0.0303]	2960[0.0305]
Completeness	100	100	100
Data/restraints/parameters	18948/1/1094	4174/0/340	2960/0/245
Goodness-of-fit on F^2	0.994	1.057	1.047
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0299, wR_2 = 0.0819	R_1 = 0.0212, wR_2 = 0.0536	R_1 = 0.0253, wR_2 = 0.0683
Final R indices [all data]	R_1 = 0.0314, wR_2 = 0.0829	R_1 = 0.0235, wR_2 = 0.0555	R_1 = 0.0271, wR_2 = 0.0699
Largest diff. peak/hole / e $Å^{-3}$	0.91/-0.58	0.47/-0.42	1.32/-0.46
Flack parameter where applicable	0.403(12)		

Table J. Crystal data and structure refinement for **3.18, 3.19** and **3.20**

Compound	3sw40 (3s) **3.18**	3sw45 (3Y) **3.19**	3sw43/3s **3.20**
Empirical formula	$C_{12}H_{15}NO_4ClAg$	$C_{11}H_{14}N_2O_4ClAg$	$C_{9.6}H_{8.2}N_3O_4ClAg$
Formula weight	380.57	381.56	372.41
Temperature	115.0	114.15	114.15
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_12_12$
Unit cell dimensions: a/Å	8.8079(4)	12.6852(4)	15.3229(9)
b/Å	12.2447(4)	8.1924(3)	21.2905(11)
c/Å	12.5250(6)	12.8192(5)	8.0381(4)
α/°	90.00	90.00	90.00
β/°	90.00	99.738(2)	90.00
γ/°	90.00	90.00	90.00
Volume/$Å^3$	1350.82(10)	1313.00(8)	2622.3(2)
Z	4	4	8
Density (calculated) Mg/m^3	1.871	1.930	1.887
Absorption coefficient mm^{-1}	1.698	1.749	1.752
F(000)	760	760	1460
Crystal size/mm^3	0.3 × 0.18 × 0.13	0.7 × 0.68 × 0.33	0.29 × 0.09 × 0.06
Theta range for data collection (°)	5.7 to 55°	5.92 to 52.88°	3.82 to 50.1°
Reflections collected	31161	26401	13441
Independent reflections [R(int)]	3097[0.0537]	2682[0.0329]	4650[0.0334]
Completeness	100	100	100
Data/restraints/parameters	3097/0/173	2682/0/172	4650/0/381
Goodness-of-fit on F^2	1.054	1.105	0.968
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0181, wR_2 = 0.0448	R_1 = 0.0216, wR_2 = 0.0564	R_1 = 0.0480, wR_2 = 0.1102
Final R indices [all data]	R_1 = 0.0190, wR_2 = 0.0451	R_1 = 0.0236, wR_2 = 0.0580	R_1 = 0.0730, wR_2 = 0.1194
Largest diff. peak/hole / e $Å^{-3}$	0.37/-0.44	0.43/-0.66	0.89/-0.55
Flack parameter where applicable	-0.037(19)		0.06(5)

Table K. Crystal data and structure refinement for **3.21, 3.22** and **3.23**

Compound	3sw42 **3.21**	3sw55 **3.22**	3s356 **3.23**
Empirical formula	$C_{22}H_{28}N_6O_7F_6S_2Ag_2$	$C_{20}H_{19}N_4O_6F_6S_4Ag_2$	$C_{15}H_{16}N_2O_4ClAg$
Formula weight	882.36	869.37	431.62
Temperature	114.15	117.15	116.15
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	P-1	$P2_1/n$
Unit cell dimensions: a/Å	11.6969(3)	7.8652(3)	12.1378(4)
b/Å	12.9740(3)	14.0587(5)	10.7654(3)
c/Å	20.0150(5)	14.8864(6)	13.2121(4)
α/°	90.00	113.746(2)	90.00
β/°	90.00	92.329(2)	111.584(2)
γ/°	90.00	90.687(2)	90.00
Volume/$Å^3$	3037.39(13)	1504.73(10)	1605.35(8)
Z	4	2	4
Density (calculated) Mg/m^3	1.930	1.919	1.786
Absorption coefficient mm^{-1}	1.516	1.658	1.443
F(000)	1752	854	864
Crystal size/mm^3	0.36 × 0.09 × 0.06	0.49 × 0.3 × 0.1	0.5 × 0.32 × 0.10
Theta range for data collection (°)	4.04 to 50.08°	5.16 to 50.1°	5.22 to 50.1°
Reflections collected	58870	26826	28656
Independent reflections [R(int)]	5366[0.0623]	5337[0.0429]	2846[0.0597]
Completeness	100	100	100
Data/restraints/parameters	5366/0/414	5337/0/516	2846/0/218
Goodness-of-fit on F^2	0.995	1.096	0.981
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0210, wR_2 = 0.0423	R_1 = 0.0367, wR_2 = 0.0999	R_1 = 0.0362, wR_2 = 0.1012
Final R indices [all data]	R_1 = 0.0237, wR_2 = 0.0431	R_1 = 0.0458, wR_2 = 0.1048	R_1 = 0.0494, wR_2 = 0.1068
Largest diff. peak/hole / e $Å^{-3}$	0.46/-0.33	0.98/-1.16	0.98/-0.45
Flack parameter where applicable	-0.022(15)		

Table L. Crystal data and structure refinement for **3.25a, 3.26** and **3.31a**

Compound	3sw70 **3.25a**	3sw44 **3.26**	3sw38 **3.31a**
Empirical formula	$C_9H_{13}NO_4Cl$	$C_{28}H_{36}N_2$	$C_{22}H_{28}N_2O_8Cl_2$
Formula weight	234.65	400.59	519.36
Temperature	117.15	114.15	114.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	Cc	$P2_1/c$
Unit cell dimensions: a/Å	8.5135(4)	17.5472(7)	10.3042(3)
b/Å	13.4741(7)	17.5839(7)	8.1092(3)
c/Å	9.7781(5)	16.5112(7)	14.6817(5)
α/°	90.00	90.00	90.00
β/°	102.991(3)	107.747(2)	95.415(2)
γ/°	90.00	90.00	90.00
Volume/$Å^3$	1092.95(9)	4852.1(3)	1221.31(7)
Z	4	8	2
Density (calculated) Mg/m^3	1.426	1.097	1.412
Absorption coefficient mm^{-1}	0.344	0.063	0.315
F(000)	492	1744	544
Crystal size/mm^3	0.3 × 0.1 × 0.08	0.30 × 0.22 × 0.12	0.61 × 0.39 × 0.35
Theta range for data collection (°)	6.04 to 53.52°	4.68 to 53°	3.98 to 55°
Reflections collected	16473	50480	26773
Independent reflections [R(int)]	2322[0.0585]	9959[0.0707]	2805[0.0289]
Completeness	99.8	99	99.9
Data/restraints/parameters	2322/0/176	9959/145/568	2805/0/166
Goodness-of-fit on F^2	1.103	0.966	1.044
Final R_1 indices [I>2sigma (I)]	$R_1 = 0.0499$, $wR_2 = 0.1058$	$R_1 = 0.0604$, $wR_2 = 0.1556$	$R_1 = 0.0324$, $wR_2 = 0.0907$
Final R indices [all data]	$R_1 = 0.0650$, $wR_2 = 0.1125$	$R_1 = 0.0908$, $wR_2 = 0.1712$	$R_1 = 0.0365$, $wR_2 = 0.0940$
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.36	0.33/-0.24	0.33/-0.35
Flack parameter where applicable		3(3)	

Table M. Crystal data and structure refinement for **3.32, 3.33** and **3.37**

Compound	3sw48 **3.32**	3sw102 **3.33**	3sw37 **3.37**
Empirical formula	$C_{18}H_{28}N_5O_{10}Cl_3Ag_2$	$C_{17}H_{20}N_5O_6F_6S_2ClAg_2$	$C_{24}H_{31}N_5O_6F_6S_2Ag_2$
Formula weight	796.54	819.69	879.40
Temperature	114.0	293(2)	112.15
Crystal system	triclinic	trigonal	monoclinic
Space group	P-1	R-3	$P2_1/c$
Unit cell dimensions: a/Å	10.9576(4)	41.519(6)	12.4040(4)
b/Å	12.0044(4)	41.519(6)	22.1684(8)
c/Å	12.1220(4)	9.1478(18)	23.4044(8)
α/°	65.317(2)	90.00	90.00
β/°	70.029(2)	90.00	97.655(2)
γ/°	76.155(2)	120.00	90.00
Volume/$Å^3$	1352.96(8)	13657(4)	6378.3(4)
Z	2	18	8
Density (calculated) Mg/m^3	1.955	1.794	1.832
Absorption coefficient mm^{-1}	1.804	1.591	1.440
F(000)	792	7236	3504
Crystal size/mm^3	0.45 × 0.26 × 0.2	0.3 × 0.12 × 0.06	0.45 × 0.4 × 0.38
Theta range for data collection (°)	5.16 to 50.1°	4.6 to 50.1°	3.32 to 51.44°
Reflections collected	25396	13776	127348
Independent reflections [R(int)]	4793[0.0474]	5354[0.0418]	12139[0.0564]
Completeness	100	99.9	99.8
Data/restraints/parameters	4793/2/350	5354/0/352	12139/0/812
Goodness-of-fit on F^2	1.054	1.046	1.074
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0313, wR_2 = 0.0785	R_1 = 0.0453, wR_2 = 0.1406	R_1 = 0.0501, wR_2 = 0.1251
Final R indices [all data]	R_1 = 0.0408, wR_2 = 0.0817	R_1 = 0.0508, wR_2 = 0.1463	R_1 = 0.0685, wR_2 = 0.1373
Largest diff. peak/hole / e $Å^{-3}$	1.20/-0.90	1.93/-0.73	3.21/-1.80

Table N. Crystal data and structure refinement for **3.38, 3.39** and **4.14**

Compound	3sw53 **3.38**	3sw50 **3.39**	3sw61 **4.14**
Empirical formula	$C_{21}H_{30}Ag_2Cl_2N_6O_8$	$C_{24}H_{30}N_6O_9F_9S_3Ag_3$	$C_{24}H_{26}N_4$
Formula weight	781.15	1137.33	370.49
Temperature	117.15	114.15	117.15
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
Unit cell dimensions: a/Å	10.4069(2)	15.8670(7)	9.6817(5)
b/Å	13.8557(4)	12.8111(5)	9.9131(4)
c/Å	37.5419(10)	18.0525(8)	10.6697(5)
α/°	90.00	90.00	90.00
β/°	90.00	93.503(2)	97.694(3)
γ/°	90.00	90.00	90.00
Volume/Å^3	5413.4(2)	3662.7(3)	1014.81(8)
Z	8	4	2
Density (calculated) Mg/m^3	1.917	2.062	1.212
Absorption coefficient mm^{-1}	1.702	1.861	0.073
F(000)	3120	2232	396
Crystal size/mm^3	0.48 × 0.3 × 0.14	0.4 × 0.29 × 0.07	0.5 × 0.3 × 0.29
Theta range for data collection (°)	4.48 to 50.1°	4.52 to 50.1°	6.74 to 55°
Reflections collected	103327	68271	22009
Independent reflections [R(int)]	9594[0.0660]	6487[0.0825]	2320[0.0434]
Completeness	99.9	99.8	99.9
Data/restraints/parameters	9594/0/703	6487/0/533	2320/0/131
Goodness-of-fit on F^2	1.048	0.970	1.083
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0366, wR_2 = 0.0853	R_1 = 0.0318, wR_2 = 0.0630	R_1 = 0.0393, wR_2 = 0.0987
Final R indices [all data]	R_1 = 0.0408, wR_2 = 0.0875	R_1 = 0.0515, wR_2 = 0.0675	R_1 = 0.0528, wR_2 = 0.1041
Largest diff. peak/hole / e Å^{-3}	2.28/-2.76	0.71/-0.55	0.18/-0.18

Table O. Crystal data and structure refinement for **4.22, 3.4.23** and **4.24**

Compound	3sw26 (3pjsp-1) **4.22**	3sw17s **4.23**	3sw79 **4.24**
Empirical formula	$C_8H_{12}N_2O_4F_3SAg$	$C_7H_{12}BN_2OF_4Ag$	$C_{13}H_{14}AgClN_2O_5$
Formula weight	397.13	334.87	421.58
Temperature	110.15	113.15	113.15
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/c$	P-1
Unit cell dimensions: a/Å	8.0040(2)	19.3527(8)	8.7979(3)
b/Å	8.3349(2)	13.8767(5)	8.8951(3)
c/Å	11.4974(3)	18.9763(7)	9.3445(3)
α/°	84.4310(10)	90.00	72.488(2)
β/°	88.8600(10)	118.192(2)	84.987(2)
γ/°	62.7950(10)	90.00	82.233(2)
Volume/$Å^3$	678.69(3)	4491.6(3)	690.15(4)
Z	2	16	2
Density (calculated) Mg/m^3	1.943	1.981	2.029
Absorption coefficient mm^{-1}	1.684	1.828	1.680
F(000)	392	2624	420
Crystal size/mm^3	0.4 × 0.34 × 0.16	0.9 × 0.28 × 0.18	0.45 × 0.32 × 0.28
Theta range for data collection (°)	5.52 to 50.1°	2.38 to 62.6°	4.58 to 55°
Reflections collected	10743	126314	15575
Independent reflections [R(int)]	2394[0.0334]	14560[0.0680]	3170[0.0355]
Completeness	99.8	99.1	99.9
Data/restraints/parameters	2394/0/191	14560/0/614	3170/0/199
Goodness-of-fit on F^2	1.067	1.192	1.119
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0171, wR_2 = 0.0424	R_1 = 0.0361, wR_2 = 0.0862	R_1 = 0.0212, wR_2 = 0.0572
Final R indices [all data]	R_1 = 0.0178, wR_2 = 0.0429	R_1 = 0.0426, wR_2 = 0.0886	R_1 = 0.0232, wR_2 = 0.0583
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.36	0.98/-1.19	0.40/-0.60

Table P. Crystal data and structure refinement for **4.25, 4.26** and **4.27**

Compound	3sw82 **4.25**	3sw81 **4.26**	3sw85_1 (3s) **4.27**
Empirical formula	$C_{14}H_{16}N_2O_5F_3SAg$	$C_{13}H_{14}BN_2OF_4Ag$	$C_{13}H_{16}AgF_6N_2O_2P$
Formula weight	489.22	408.94	485.12
Temperature	113.15	112.15	293(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
Unit cell dimensions: a/Å	8.9647(3)	8.3701(3)	8.5059(5)
b/Å	10.7915(4)	16.7017(5)	9.5738(6)
c/Å	18.1858(6)	10.0532(3)	10.4942(6)
α/°	90.00	90.00	92.382(4)
β/°	96.909(2)	96.754(2)	105.339(3)
γ/°	90.00	90.00	101.690(4)
Volume/$Å^3$	1746.57(10)	1395.63(8)	802.94(8)
Z	4	4	2
Density (calculated) Mg/m^3	1.860	1.946	2.007
Absorption coefficient mm^{-1}	1.333	1.491	1.430
F(000)	976	808	480
Crystal size/mm^3	0.26 × 0.16 × 0.14	0.49 × 0.4 × 0.15	0.48 × 0.44 × 0.39
Theta range for data collection (°)	5.34 to 50.08°	4.76 to 54.98°	6.24 to 50.1°
Reflections collected	32969	31314	14991
Independent reflections [R(int)]	3092[0.0678]	3192[0.0366]	2842[0.0540]
Completeness	99.8	100	99.8
Data/restraints/parameters	3092/2/243	3192/0/227	2842/0/228
Goodness-of-fit on F^2	1.124	1.050	0.922
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0330, wR_2 = 0.0792	R_1 = 0.0186, wR_2 = 0.0485	R_1 = 0.0353, wR_2 = 0.0863
Final R indices [all data]	R_1 = 0.0427, wR_2 = 0.0820	R_1 = 0.0216, wR_2 = 0.0497	R_1 = 0.0407, wR_2 = 0.0886
Largest diff. peak/hole / e $Å^{-3}$	0.61/-0.52	0.45/-0.55	1.75/-0.84

Table Q. Crystal data and structure refinement for **4.28, 4.29** and **4.30**

Compound	3sw23 **4.28**	3sw69_1 **4.29**	3sw65 **4.30**
Empirical formula	$C_9H_{16}O_3F_3SiSAg$	$C_{12}H_{17}N_3O_4F_6PAg$	$C_{12}H_{15}N_4O_6Ag$
Formula weight	397.24	520.13	419.15
Temperature	107.15	115.15	118.15
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/n$	$P2_1/n$
Unit cell dimensions: a/Å	9.0680(4)	13.4115(6)	7.3854(4)
b/Å	9.0951(4)	9.7327(4)	13.9710(6)
c/Å	9.2479(5)	13.4746(7)	15.3168(7)
α/°	81.531(3)	90.00	90.00
β/°	74.879(3)	93.890(3)	99.910(3)
γ/°	89.931(3)	90.00	90.00
Volume/$Å^3$	727.73(6)	1754.79(14)	1556.83(13)
Z	2	4	4
Density (calculated) Mg/m^3	1.813	1.969	1.788
Absorption coefficient mm^{-1}	1.640	1.326	1.331
F(000)	396	1032	840
Crystal size/mm^3	0.22 × 0.13 × 0.1	0.25 × 0.1 × 0.06	0.4 × 0.25 × 0.13
Theta range for data collection (°)	5.62 to 50.1°	5.9 to 54.18°	5.78 to 53.86°
Reflections collected	14150	36845	32455
Independent reflections [R(int)]	2570[0.0706]	3819[0.1002]	3346[0.0688]
Completeness	99.8	98.6	99
Data/restraints/parameters	2570/0/172	3819/0/252	3346/0/227
Goodness-of-fit on F^2	0.797	0.899	1.087
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0289, wR_2 = 0.0658	R_1 = 0.0381, wR_2 = 0.0691	R_1 = 0.0339, wR_2 = 0.0781
Final R indices [all data]	R_1 = 0.0357, wR_2 = 0.0693	R_1 = 0.0625, wR_2 = 0.0748	R_1 = 0.0460, wR_2 = 0.0808
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.72	0.79/-0.76	0.94/-0.65

Table R. Crystal data and structure refinement for **4.31, 4.32** and **4.33**

Compound	3sw28 **4.31**	3sw31 (3s) **4.32**	3sw32 (3pjs3) **4.33**
Empirical formula	$C_{13}H_{20}N_2O_9Cl_2Ag_2$	$C_{17}H_{22}N_2O_{14}F_{12}S_4Ag_4$	$C_{13}H_{28}B_2\ N_2O_5F_8Ag_2$
Formula weight	634.95	1266.09	681.73
Temperature	110.15	112.0	113.15
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12$	C2/c	Fdd2
Unit cell dimensions: a/Å	8.3985(3)	24.2984(7)	18.4679(5)
b/Å	15.0933(5)	11.5154(3)	31.8923(9)
c/Å	7.8538(2)	15.6844(4)	7.8966(2)
α/°	90.00	90.00	90.00
β/°	90.00	124.6650(10)	90.00
γ/°	90.00	90.00	90.00
Volume/$Å^3$	995.56(5)	3609.57(17)	4651.0(2)
Z	2	4	8
Density (calculated) Mg/m^3	2.118	2.330	1.947
Absorption coefficient mm^{-1}	2.284	2.492	1.774
F(000)	624	2440	2688
Crystal size/mm^3	0.55 × 0.47 × 0.28	0.72 × 0.52 × 0.4	0.68 × 0.58 × 0.38
Theta range for data collection (°)	5.18 to 55°	5.22 to 55°	5.1 to 50.08°
Reflections collected	42471	39696	26555
Independent reflections [R(int)]	2285[0.0288]	4144[0.0315]	2043[0.0304]
Completeness	100	100	99.9
Data/restraints/parameters	2285/0/129	4144/0/281	2043/1/191
Goodness-of-fit on F^2	1.229	1.023	1.037
Final R_1 indices [I>2sigma (I)]	R_1 = 0.0123, wR_2 = 0.0331	R_1 = 0.0306, wR_2 = 0.0880	R_1 = 0.0132, wR_2 = 0.0332
Final R indices [all data]	R_1 = 0.0144, wR_2 = 0.0333	R_1 = 0.0353, wR_2 = 0.0923	R_1 = 0.0134, wR_2 = 0.0333
Largest diff. peak/hole / e $Å^{-3}$	0.50/-0.75	1.88/-1.50	0.23/-0.34
Flack parameter where applicable	0.522(18)		0.12(2)

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